



Chemical Speciation Analysis and Environmental Behaviour of ^{127}I and ^{129}I

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Publication date:
2011

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):
Hansen, V. (2011). *Chemical Speciation Analysis and Environmental Behaviour of ^{127}I and ^{129}I* . Risø National Laboratory. Risø-PhD No. 81(EN)

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Chemical Speciation Analysis and Environmental Behaviour of ^{127}I and ^{129}I

Risø-PhD-Report

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Risø-PhD-81(EN)
October 2011

Risø DTU
National Laboratory for Sustainable Energy



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Title: Chemical Speciation Analysis and Environmental Behaviour of ^{127}I and ^{129}I

Division: Radiation Research

Risø-PhD-81(EN)

October 2011

This thesis is submitted in fulfilment of requirements for the Ph. D. degree at Risø National Laboratory for Sustainable Energy, Technical University of Denmark.

Abstract:

This thesis deals with chemical speciation analysis and behaviour of the anthropogenic radioisotope ^{129}I as well as stable iodine ^{127}I in environmental samples such as freshwater, seawater, soils, sediments and seaweed. The behaviour and chemical speciation of iodine (^{127}I and ^{129}I) in environmental samples are very complex and strongly dependent on several factors, such as water/soil/sediment chemistry, seaweed type, different pH, E_h , quantity and quality of organic matter, microbiological activity as well as differences in contaminant origin. The ^{129}I isotope, where the main inventory has been present in the biosphere for a relatively short time, may not show the same behaviour as the stable ^{127}I isotope. The present study illustrates this.

Chemical speciation analysis of ^{129}I and ^{127}I as iodide, iodate and total inorganic iodine in seawater samples from the Baltic Proper, Skagerrak and Kattegat has been carried out. The general trend in variability of the iodide and iodate speciation of the two iodine isotopes is, to a large extent, linked to environmental conditions. The important findings of this study are that the reduction of iodate and oxidation of iodide in Skagerrak and Kattegat may be a slow process while along the Baltic Sea surface water reduction of iodate is a relatively fast process. Although suboxic or anoxic conditions are encountered in some of the Baltic Sea deep basins, the concentration of $^{129}\text{IO}_3^-$ increases with water depth indicating that the reduction of iodate in the oxygen deficient bottom water of the Baltic Sea is a slow process.

Iodine chemical speciation analysis (as iodide, iodate and total iodine including inorganic and organic iodine species) in lake water samples collected from Denmark and southern Sweden has been carried out. Destruction of organic iodine was performed by alkaline oxidation using $\text{NaOH} - \text{NaClO}$ at 100°C and anion exchange chromatography was used for separation of iodide and iodate. Iodine-129 concentrations in the lakes ranged from $1.3 - 12.8 \times 10^9$ at/L and show elevated concentrations in lakes located in southwest Jutland (Denmark), near the North Sea. Except the Skærsø Lake, where the organic iodine – 127 accounts for 50% of the total iodine, iodide (both ^{129}I and ^{127}I) is the predominant species form in surface water of the studied lakes.

An investigation was conducted in order to quantify the total aquatic iodine (^{129}I and ^{127}I as inorganic and organic iodine) from fresh water and seawater samples by adsorption onto activated charcoal and DEAE 32 cellulose followed by alkaline digestion or combustion. The results show that iodide from freshwater samples can easily be adsorbed onto activated charcoal. The sorption was not affected by the pH. The absorption capacity of iodate is low and reduces quickly when its concentration increases. Compared with activated charcoal, DEAE 32 cellulose showed a lower adsorption capacity of inorganic and organic iodine species. Adsorption of iodine species onto activated charcoal and DEAE 32 cellulose from seawater samples shows that only about 10% of the total iodine in seawater can be adsorbed onto those materials. Adsorption of iodine species from water samples onto activated charcoal/DEAE is not a suitable method for quantifying the total iodine in freshwater and seawater.

An investigation was conducted in order to decompose organic iodine using $\text{K}_2\text{S}_2\text{O}_8$ in water samples for developing a method for quantification of aquatic organic iodine (^{129}I and ^{127}I). The results show that iodine was quantitatively removed even when the concentration of organic iodine compounds in the studied sample was very high. Due to this, oxidation of iodine organic matter by using $\text{K}_2\text{S}_2\text{O}_8$ followed by reduction of iodine species and precipitation with silver can be a potential method for determination of total iodine in fresh water samples.

An improvement was made of the method for ^{129}I and ^{127}I speciation analysis in soil and sediment samples involving the extraction and fractionation of organic matter. The improved method was further used for the partitioning of ^{127}I and ^{129}I in marine sediments and soils. Sequential extraction results point out that partitioning of ^{127}I and ^{129}I within the organic fraction in soil and marine sediments is controlled by pH conditions where pH values below 5.0-5.5 promote occurrence of ^{127}I and ^{129}I in the humic acid, while at $\text{pH} > 6$ the partitioning was in the fulvic acid fraction. Anoxic conditions seemed to increase the mobility and availability of iodine compared to oxic, while suboxic conditions (soils) reduced the availability of the water soluble fraction compared to the subaqueous (marine) one. The distribution of $^{129}\text{I}/^{127}\text{I}$ values differed significantly between phases and samples, indicating that equilibrium with stable iodine have not yet been reached for a large fraction of the released ^{129}I . This means that geochemical models based on stable iodine behavior may not necessarily be able to predict the present behavior of ^{129}I .

Concentrations of ^{129}I and ^{127}I in archived *Fucus Vesiculosus* samples collected between 2002 – 2010 at Romø (German Bight), Klint (Kattegat) and Bornholm were analysed. Since previous investigations have shown that iodine speciation differ between the sites a comparison between $^{129}\text{I}/^{127}\text{I}$ ratios in seaweed relative to water at the three sites were done in order to evaluate if uptake was independent on speciation. The $^{129}\text{I}/^{127}\text{I}$ (seaweed) relative $^{129}\text{I}/^{127}\text{I}$ (seawater) were found to be 0.5 for the North Sea (2005), 0.7 (2006) for Southern Kattegat and 0.97 (2007) for Bornholm. In spite of the very different iodine speciation at the three sites the concentration ratio seaweed to water is more or less the same indicating that *Fucus Vesiculosus* can be used as a bio-indicator for iodine-129 in the marine environment. The results shows however that iodide is somewhat more efficient accumulate than iodate in *Fucus*.

A rapid on-line HPLC-ICP-MS method for direct speciation analysis of ^{127}I (as iodide and iodate) in water samples was developed. The method was further used for the speciation analysis of ^{127}I in freshwater and seawater (following dilution). The results demonstrate that the on-line HPLC – ICP – MS method developed in this study is reliable and efficient for accurate assay for speciation analysis of stable iodine in water samples. Due to the low concentrations of ^{129}I in the environment the HPLC-ICP-MS method cannot be applied for speciation analysis of this isotope in environmental samples but can be applied for water samples highly contaminated with ^{129}I .

ISBN 978-87-550-3889-9

Pages:175

Tables:10

References:106

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Thesis for the Degree of Doctor of Philosophy
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Chemical Speciation Analysis and Environmental Behaviour of ^{127}I and ^{129}I

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To be presented with the permission of the Radiation Research Division for public criticism in Risø-DTU,
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Abstract

This thesis deals with chemical speciation analysis and behaviour of the anthropogenic radioisotope ^{129}I as well as stable iodine ^{127}I in environmental samples such as freshwater, seawater, soils, sediments and seaweed. The behaviour and chemical speciation of iodine (^{127}I and ^{129}I) in environmental samples are very complex and strongly dependent on several factors, such as water/soil/sediment chemistry, seaweed type, different pH, E_h , quantity and quality of organic matter, microbiological activity as well as differences in contaminant origin. The ^{129}I isotope, where the main inventory has been present in the biosphere for a relatively short time, may not show the same behaviour as the stable ^{127}I isotope. The present study illustrates this.

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An investigation was conducted in order to quantify the total aquatic iodine (^{129}I and ^{127}I as inorganic and organic iodine) from fresh water and seawater samples by adsorption onto activated charcoal and DEAE 32 cellulose followed by alkaline digestion or combustion. The results show that iodide from freshwater samples can easily be adsorbed onto activated charcoal. The sorption was not affected by the pH. The absorption capacity of iodate is low and reduces quickly when its concentration increases. Compared with activated charcoal, DEAE 32 cellulose showed a lower adsorption capacity of inorganic and organic iodine species. Adsorption of iodine species onto activated charcoal and DEAE 32 cellulose from seawater

samples shows that only about 10% of the total iodine in seawater can be adsorbed onto those materials. Adsorption of iodine species from water samples onto activated charcoal/DEAE is not a suitable method for quantifying the total iodine in freshwater and seawater.

An investigation was conducted in order to decompose organic iodine using $K_2S_2O_8$ in water samples for developing a method for quantification of aquatic organic iodine (^{129}I and ^{127}I). The results show that iodine was quantitatively removed even when the concentration of organic iodine compounds in the studied sample was very high. Due to this, oxidation of iodine organic matter by using $K_2S_2O_8$ followed by reduction of iodine species and precipitation with silver can be a potential method for determination of total iodine in fresh water samples.

An improvement was made of the method for ^{129}I and ^{127}I speciation analysis in soil and sediment samples involving the extraction and fractionation of organic matter. The improved method was further used for the partitioning of ^{127}I and ^{129}I in marine sediments and soils. Sequential extraction results point out that partitioning of ^{127}I and ^{129}I within the organic fraction in soil and marine sediments is controlled by pH conditions where pH values below 5.0-5.5 promote occurrence of ^{127}I and ^{129}I in the humic acid, while at pH > 6 the partitioning was in the fulvic acid fraction. Anoxic conditions seemed to increase the mobility and availability of iodine compared to oxic, while suboxic conditions (soils) reduced the availability of the water soluble fraction compared to the subaqueous (marine) one. The distribution of $^{129}I/^{127}I$ values differed significantly between phases and samples, indicating that equilibrium with stable iodine have not yet been reached for a large fraction of the released ^{129}I . This means that geochemical models based on stable iodine behavior may not necessarily be able to predict the present behavior of I-129.

Concentrations of ^{129}I and ^{127}I in archived *Fucus Vesiculosus* samples collected between 2002 – 2010 at Romø (German Bight), Klint (Kattegat) and Bornholm were analysed. Since previous investigations have shown that iodine speciation differ between the sites a comparison between $^{129}I/^{127}I$ ratios in seaweed relative to water at the three sites were done in order to evaluate if uptake was independent on speciation. The $^{129}I/^{127}I$ (seaweed) relative $^{129}I/^{127}I$ (seawater) were found to be 0.5 for the North Sea (2005), 0.7 (2006) for Southern Kattegat and 0.97 (2007) for Bornholm. In spite of the very different iodine speciation at the three sites the concentration ratio seaweed to water is more or less the same indicating that *Fucus Vesiculosus* can be used as a bio-indicator for iodine-129 in the marine environment. The results shows however that iodide is somewhat more efficient accumulate than iodate in *Fucus*.

Concentrations of ^{129}I and ^{127}I in fifty archived *Fucus Vesiculosus* samples (collected over a period starting in 2002) were analysed. Yields ratios of $^{129}I/^{127}I$ (seaweed) relative $^{129}I/^{127}I$ (seawater) were found to be 0.5 for North Sea (2005), 0.7 (2006) for Southern Kattegat and 0.97 (2007) for Bornholm indicating that *Fucus Vesiculosus* can be used as bio-indicator organisms for iodine-129 in marine

environment since they reflect the iodine-129 discharge from reprocessing facilities. The results further show that the iodide is more efficient to accumulate than iodate in Fucus.

A rapid on-line HPLC-ICP-MS method for direct speciation analysis of ^{127}I (as iodide and iodate) in water samples was developed. The method was further used for the speciation analysis of ^{127}I in freshwater and seawater (following dilution). The results demonstrate that the on-line HPLC – ICP - MS method developed in this study is reliable and efficient for accurate assay for speciation analysis of stable iodine in water samples. Due to the low concentrations of ^{129}I in the environment the HPLC-ICP-MS method cannot be applied for speciation analysis of this isotope in environmental samples but can be applied for water samples highly contaminated with ^{129}I .

Abstract in Danish

Emnet for denne afhandling er kemisk specierings analyse og opførsel af den antropogene radioisotop ^{129}I og stabilt jod ^{127}I i miljøprøver, såsom ferskvand, havvand, jord, sedimenter og tang.

Opførslen og den kemiske speciering af jod (^{127}I og ^{129}I) i miljøprøver, såsom ferskvand, havvand, sedimenter, jord og tang er særdeles kompleks, og afhænger kraftigt af en mængde faktorer, heriblandt vand/jord/sediment-kemi, tangtype, forskelle i pH, Eh, mængder og typer af organisk materiale, mikrobiologisk aktivitet, forskelle i oprindelsen af kontamineringen og kemisk speciering af begge isotoper, samt vandmassetransport.

Kemisk specieringsanalyse er udført til identifikation af ^{129}I og ^{127}I på jodid- og jodat form samt totalt inorganisk jod indhold i havvandsprøver fra Østersøen, Skagerrak og Kattegat. Variationen i jodid- og jodatspecieringen af de to jodisotoper er for en stor dels vedkommende forårsaget af miljømæssige parametre. De væsentligste resultater af denne undersøgelse er, at reduktionen af jodat og oxideringen af jodid i Skagerrak og Kattegat kan være langsommelige processer, hvorimod reduktionen af jodat i overfladevand i Østersøen foregår relativt hurtigt. På trods af suboxiske eller anoxiske forhold i dybvand nogle steder i Østersøen, øges koncentrationen af $^{129}\text{IO}_3^-$ med vanddybden, hvilket indikerer, at reduktionen af jodat i anoksisk bundvand i Østersøen er en langsom proces.

Kemisk speciering af jod (som jodid, jodat, og total jod inklusive inorganiske og organiske jodformer) er analyseret i søvandsprøver fra Danmark og Sydsverige. Nedbrydning af organisk jod udførtes ved basisk oxidering under anvendelse af NaOH – NaClO ved 100°C og separationen i jodid og jodat foregik ved anjonbytter-kromatografi. Jodkoncentrationen i søer varierede mellem $1.3 - 12.8 \times 10^9$ at/L, med forhøjede koncentrationer i områder i Sydvestjylland, nær Nordsøen. Med undtagelse af Skærsø, hvor den organiske jod-127 udgør halvdelen af den totale jod, er jodid (både ^{129}I and ^{127}I) den dominerende form i overfladevand fra de undersøgte søer. Den organiske jodfraktion er muligvis undervurderet, delvist på grund af nedbrydning af NaClO i forbindelse med forhøjelse af temperaturen (i denne undersøgelse 150°C i 3 timer). Af denne årsag er en del af den organiske jod i disse prøver muligvis ikke blevet nedbrudt og derfor ikke indeholdt i den totale jodkoncentration i de undersøgte prøver.

En undersøgelse havde til formål at kvantificere den total akvatiske jodkoncentration (^{129}I og ^{127}I som inorganisk og organisk jod) i ferskvandsprøver og havvandsprøver ved adsorption på aktivt kul og DEAE 32 cellulose, efterfulgt af alkalisk nedbrydning eller forbrænding. Resultaterne viser, at jodid fra ferskvandsprøver let adsorberes på aktivt kul vasket i dobbelt destilleret vand. Sorptionen påvirkedes ikke af pH. Absorptionskapaciteten for jodat er lav og reduceres hurtigt, når jodatkoncentrationen forøges. Sammenlignet med aktivt kul havde DEAE 32 cellulose en ringere adsorptionskapacitet for inorganiske og

organiske jodformer. Adsorption af jodformer på aktivt kul og DEAE 32 cellulose fra havvandsprøver viser, at kun 9% af den totale jod i havvand kan adsorberes på disse materialer. Adsorption af jodformer fra vandprøver på aktivt kul/DEAE er ikke en anvendelig metode til kvantificering af total jod i ferskvand og havvand.

Muligheden for at nedbryde organisk jod i vandprøver ved anvendelse af $K_2S_2O_8$ undersøgtes med det formål at udvikle en metode til kvantificering af akvatisk organisk jod (^{129}I og ^{127}I). Resultaterne viser, at jod kvantitativt fjernedes, selv når koncentrationen af organiske jodformer i prøven var meget høj. Oxidering af organisk jod ved brug af $K_2S_2O_8$, efterfulgt af reduktion af jodformerne og udfældning med sølvnitrat, kan derfor være en mulig teknik til totalbestemmelse af jod i ferskvandsprøver. Fordi flere prøver kan behandles samtidigt, er metoden hurtig og velegnet til in situ separation ombord på forskningsfartøjer.

Metoden til specieringsanalyse af ^{129}I og ^{127}I i jord- og sedimentprøver ved ekstraktion og fraktionering af organisk indhold forbedredes. Den forbedrede metode blev endvidere anvendt til udskilning af ^{127}I og ^{129}I i marine sedimenter og jordprøver. Resultater af sekventiel ekstraktion viser, at udskilningen af ^{127}I og ^{129}I i den organiske fraktion i jord og marine sedimenter kontrolleres af pH, hvor pH værdier under 5.0-5.5 giver forøget forekomst af ^{127}I og ^{129}I i humussyre, hvorimod pH-værdier højere, end 6 fører til opkoncentrering i den fulviske syrefraktion. Anoxiske forhold lod til at øge mobiliteten og tilgængeligheden af jod sammenlignet med oxiske forhold, hvorimod suboxiske forhold (jord) reducerede tilgængeligheden af den vandopløselige fraktion sammenlignet med den subakvatiske (marine). Fordelingen af forholdet $^{129}I/^{127}I$ varierede betydeligt mellem faser og prøver, hvilket indikerer, at ligevægt med stabilt jod endnu ikke var opnået for en stor del af den frigivne ^{129}I . Dette betyder, at geokemiske modeller baseret på opførslen af stabilt jod muligvis ikke er velegnede til at forudsige den nuværende opførsel af ^{129}I .

Der blev foretaget analyser af koncentrationer af ^{129}I og ^{127}I i 50 arkiverede *Fucus Vesiculosus* prøver (indsamlet over en årrække startende i 2002). Udbytteforholdet af $^{129}I/^{127}I$ (tang) relativt til $^{129}I/^{127}I$ (havvand) blev målt til 0.5 i Nordsøen (2005), 0.7 i det sydlige Kattegat (2006), og 0.97 ved Bornholm (2007), hvilket indikerer, at *Fucus Vesiculosus* kan anvendes som bioindikator-organisme for ^{129}I -udledninger fra oparbejdelsesanlæg. Resultaterne viser yderligere, at jodid akkumulerer mere effektivt i *Fucus*, end jodat.

En hurtig on-line HPLC-ICP-MS-metode til direkte specieringsanalyse af ^{127}I (som jodid og jodat) i vandprøver blev også udviklet. Denne metode anvendtes til specieringsanalyse af ^{127}I i ferskvand og havvand. Resultaterne viser, at den udviklede on-line HPLC – ICP – MS metode er pålidelig og effektiv til nøjagtig bestemmelse af stabile jodformer i vand og udvaskninger fra jord- og sedimentprøver. På grund af de lave ^{129}I -koncentrationer i miljøet kan HPLC-ICP-MS-metoden ikke anvendes til specieringsanalyse for antropogen jod i miljøprøver, hvorimod den kan anvendes til kraftigt ^{129}I -kontaminerede vandprøver.

Acknowledgements

I would like to acknowledge to the following, for helping directly and indirectly with this thesis:

This PhD thesis could not have been made without the help and tremendous support of my supervisor **Per Roos**. I will like to express my deepest gratitude for his professional guidance during my PhD study. I thank him for supporting me in finishing this work, for always helping and encouraging me to go on even if things do not go as expected, for sharing his analytical skills with me, for what he taught me about ICP-MS, for teaching me how to see the science in an attractive way. From his special, pleasant and skilled personality I have learnt things that I will carry with me all my life.

In particular, I want to express my gratitude to Senior Scientist **Ala Aldahan** for collaboration in the late period, and response to all my scientific writing stuff. He encouraged me to go on, even when things felt a little challenging.

I owe special thanks to **Sven P. Nielsen**, Head of Radioecology and Tracers Programme, Radiation Research Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, for helping me always and particularly in difficult moments.

Many thanks go to **Susan Zumbach Johannesen**, PhD Programme from DTU, for always being there when I need her, for always finding the best solutions for me and for always being so kindly.

My sincere appreciations go to **Jussi Jernström** for spending time on discussing my questions and helping me with the HPLC-ICP-MS analysis and **Kasper G. Andersson** for all his constructive comments to all my scientific writing stuff. His friendly and never ending positive attitude has always encouraged me in this work.

Especially thanks go to friends **Sorin P. Aburel**, **Lars R. Lindvold** and **Hedi S. Pedersen** for support, constructive comments to scientific writing stuff and always interesting discussions in the office/laboratory.

I'd also like to thank my office/building mates **Christina Ankjærgaard**, **Keliang Shi**, **Jixin Qiao**, **Peng He**, for the nice working atmosphere.

Thanks to all my colleagues from Radiation Research Division and especially to those from the Radioecology and Tracers Programme for collaboration, answers to my questions and all happy moments. Among them I will mention **Liga Bech**, **Lise Brandt**, **Susanne Kjørulff**, **Charlotte R. Mikkelsen**, **Kristina W. Veirø**, **Yu Yixuan**, **Yusuf M. Abdirahman**, **Jytte L. Clausen**, **Birgitte Sindholt**, **Svend Olsen** and **Claus Bang**.

None of this would have been possible without the love and support of my family. I thank my parents (*Daniela and Marin*), my uncle *Marian*, my beloved nephew *Patrick*, sisters (*Elena* and *Natalia*) and brother (*Raul*) and their families, my mother in law (*Lis*) for supporting and encouraging me during all those years. And finally I thank *Alexander S. Hansen and Peter Hansen* for sharing every up and down moment. Their support and understanding mean the entire world to me.

List of publications

This thesis is based on the following papers:

- I. Hou, X.L., Hansen, V., Aldahan, A., Possnert, G., Lind, O.C., Lujaniene, G., 2009. A review on speciation of iodine-129 in the environmental and biological samples. *Analytica Chimica Acta*. 632, 181-196
- II. Yi P, Aldahan A, Hansen V, Possnert G, Hou XL. Iodine Isotopes (^{129}I and ^{127}I) in the Baltic proper, Kattegat and Skagerrak Basins. *Environ. Sci. Technol.* 2011, 45, 903-909
- III. Hansen,V., Yi, P., Hou, X., Roos, P., Aldahan, A., Possnert, G. Iodine (^{129}I and ^{127}I) speciation in the surface water of Baltic Sea. Submitted to *Science of the Total Environment*
- IV. Hansen,V., Roos, P., Aldahan, A., Hou, X., Possnert, G. Partition of Iodine (^{129}I and ^{127}I) Isotopes in Soil and Sediment. Accepted for publication in *Journal of Environmental Radioactivity*.
- V. Hansen Violeta & Roos Per. 2011. Spatial and temporal variation of ^{129}I and ^{127}I by analysis of archived *Fucus Vesiculosus* samples from Denmark, Manuscript
- VI. Hansen Violeta. 2011. Iodine (^{129}I and ^{127}I) speciation in freshwater samples from Denmark and Sweden, Manuscript

Abbreviations and acronyms

b+ - positron emission

a - alpha

EC - electron capture

AMS - accelerator mass spectrometry

LSC – liquid scintillation counting

RNAA - radiochemical neutron activation analysis

NAA - neutron activation analysis

XANES - X- ray absorption near-edge structure

EXAFS - extended X- ray absorption fine structure spectra

ICP - MS - inductively coupled plasma mass spectrometry

DRC - ICP-MS - dynamic reaction cell inductively coupled plasma mass spectrometry

HPLC - high performance liquid chromatography

HPLC - CSSWV - high performance liquid chromatography coupled with cathodic stripping square wave voltammetry detection

UV - ultraviolet detection

TMAH - Tetramethylammonium hydroxide

Bio - Rad AG1 × 4 - strongly basic anion exchange resin

AC - activated charcoal

DEAE - Diethylaminoethyl

PUREX - plutonium uranium extraction

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1. Introduction

1.1 Iodine in nature

1.1.1 Stable iodine (^{127}I)

In 1811 the French chemist Bernard Courtois discovered iodine by a fortuitous accident when he sublimed the element from seaweed ash with sulphuric acid. The name comes from a Greek word for "violet colored". Due to the multiple oxidation states -1,0,+1,+3, +5 and +7 (Table 1) and an oxide IO_2 with an oxidation state of +4 its chemistry in aqueous solutions is quite complex (Figure 1). Except the oxide IO_2 (+4), all above forms are thermodynamically stable.

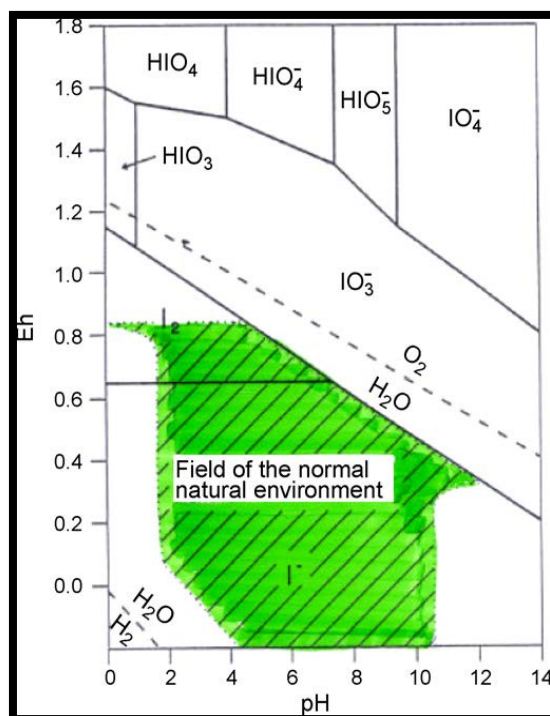


Fig. 1 Eh–pH diagram for iodine in water at 25 °C. This figure is reproduced from Liu & Gunten, 1988 and Michel, et al., 2004.

In the earth's surface environments such as oceans and seas, iodine concentration ranges between 40 and 65 $\mu\text{g/l}$ (Buraglio, 2000a). In seawater iodine exists mainly as iodide (-1), iodate (+5) and to a lesser extent as organic iodine (Wong and Zhang, 2003; Wong, 1991), Figure 2. In oxic marine waters iodate is the thermodynamically stable form, while in anoxic seawater, such as the deep waters of the Black Sea and parts of the Baltic Sea, iodide should constitute the major species of iodine (**in Paper I**; Tian and Nicolas, 1995).

Table 1 Some properties of iodine

Property	
Atomic number	53
Atomic mass	126.9045
Color	Bluish black for solid, varies with solvent for liquid and violet for gas
Electronic configuration	[Kr] 4d ¹⁰ 5s ² 5p ⁵
Oxidation states	-1 (KI); 0 (I ₂ , I ₃ ⁻ , I ₅ ⁻); +1 (IO ⁻ (hypoiodite), ICl ₂ ⁻); +3 (IO ₂ ⁻ (iodite), ICl ₃); +4 (IO ₂); +5 (I ₂ O ₅ , HIO ₃ , KIO ₃ , IF ₅ , IF ₆ ⁻); +7 (H ₅ IO ₆ , H ₄ IO ₆ ⁻ , HIO ₄ , IO ₄ ⁻ (periodate), IF ₇)
Electron affinity at 298 ⁰ K	79.0 (kcal)
Density near room temperature	4.93g cm ⁻³
Melting point	113.7 °C,
Boiling point	184.3 °C,
Atomic radius	140pm
Covalent radius	139pm
van der Walls's radius	198pm
Cristal structure, 4 mol of I ₂	Orthorhombic
pm-picometre	

The reasons for the existence of iodide in oxic surface seawater and the occurrence of iodate in anoxic water are still unclear and are somewhat of an enigma. The oxidation/reduction of inorganic iodine (Tsunogai and Sase, 1969; Tian and Nicolas, 1995; Spokes and Liss 1996; Campos et al., 1999; Amachi et al., 2004) in the marine environment was previously studied. Attempts to explain the reduction of iodate to iodide in seawater have demonstrated (Tsunogai and Sase, 1969) that certain organisms enzymatically (nitrate-reductase) are able to reduce iodate to iodide, while another study (Waite, and Truesdale, 2003) has been unable to confirm this. Campos et al., (1999) indicated that there might be a linkage between the iodide production and nitrate concentration, showing that the iodide levels increased as nitrate concentrations decreased. Through observations of the iodate-iodide redox behavior in North Sea surface water samples, Spokes et al., (1996) showed that iodide is photochemically produced by iodate reduction and that organic matter plays an important role in the process. Under prevailing conditions in seawater the oxidation of iodide to iodate is an extremely slow process (Hou, et al., 2007). The formation of volatile organic iodine in marine environments via aqueous photochemistry between dissolved organic compounds and inorganic iodine species (Moore & Zafiriou 1994; Martino et al. 2009), through chemical oxidation process, involving iodine organic matters in sediments (Keppler et al., 2000) and by macroalgae and seaweed (Leblanc et al., 2006; Francoise et al., 2008) have been reported. In seaweed the speciation and concentration of iodine vary with type/species (Leblanc et al., 2006) as well as the region in which they are found (Shah et al., 2005) and concentrations range between 10 and 2500 mg/kg (Whitehead, 1984). Between 9 and 99% of iodine in seaweed is water-soluble and occurs both as inorganic and organic species. While iodine associates with both high and low molecular weight organic compounds (Shah et al., 2005), iodide seemed to be the

predominant inorganic species (Shah et al., 2005; Küpper et al. 2008; **in Paper I**). It has been demonstrated that phytoplankton, macroalgae and seaweed accumulate iodine from seawater and oceans and transform a part of it into volatile organic iodine (VOI), such as methyl iodide (CH_3I) or diiodomethane (CH_2I_2 ; Carpenter et al. 2007) and release them in seawater. The volatile organic iodine so formed are then released from seawater surface to atmosphere. In the atmosphere the iodine concentration ranges between 1 and 100 ng/m^3 (**in Paper I**) and exists as particle-bound iodine, inorganic gaseous iodine (I_2 , HI, HOI) and organic gaseous iodine (CH_3I , CH_2I_2 , $\text{C}_3\text{H}_7\text{I}$). The concentration of all different species varies with location, season and climate (Gabler & Heumann, 1993). In the atmosphere volatile organic iodine compounds are broken down by photolysis and reactions with ozone (O_3) (Jones & Carpenter, 2005; Martino et al. 2006) forming a reactive pool of iodine species (i.e., I^\bullet , IO, HOI, I_2O_2 , IO_2), some as aerosols which eventually initiate cloud condensation (von Glasow 2005) and subsequent redistribution onto the earth's surface environment by precipitation (Figure 2).

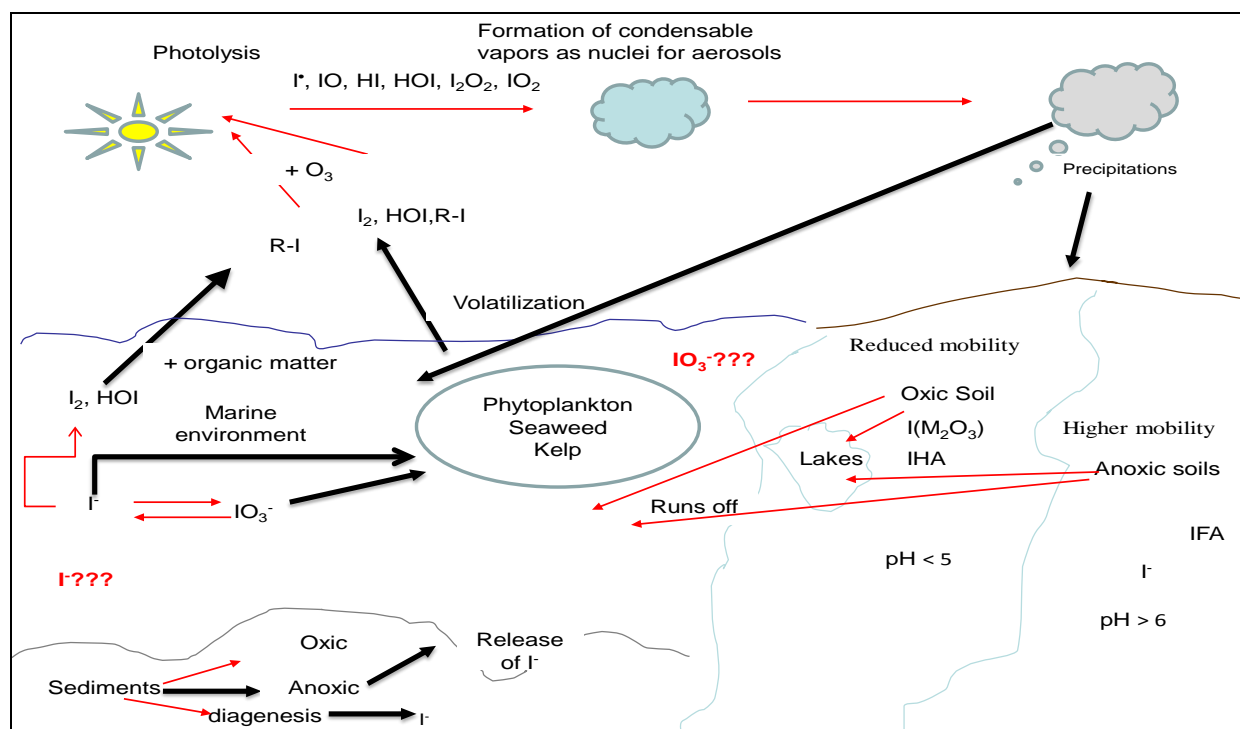


Fig. 2 Global cycle of iodine in the environment

IFA-iodine fulvic acid; IHA- iodine humic acid; $\text{I}(\text{M}_2\text{O}_3)$ - iodine associate oxides

The concentration of iodine in freshwater is with a few exceptions much lower than in seawater. In precipitation, snow, river and lake water iodine normally occurs within the range of 0.5-20 $\mu\text{g/l}$ (Whitehead, 1984) and may exist as iodide, iodate and organic iodine, with higher concentration of organic iodine compared to seawater (Reifenhäuser and Heumann, 1990).

In soils/sediments iodine occurs as organic and inorganic species depending on soil/sediment type, pH, Eh, quantity and quality of organic matter, microbiological activity, soil matrix composition itself as well as differences in contaminant origin and chemical speciation of both isotopes (^{127}I & ^{129}I) deposited on the soil/sediment (**in Paper IV**; Englund, et al., 2010; Schlegel, et al., 2006; Sheppard and Thibault, 1992). Results of speciation analysis in such reservoirs reveal that a considerable part of iodine is adsorbed on oxides and hydroxides of iron and manganese, and that most of the iodine is associated with organic matter (Hou, et al., 2003, Englund, et al., 2010; Schlegel, et al., 2006; Sheppard and Thibault, 1992; **Paper IV**). In sedimentary rocks the iodine concentrations range between 0.2 and 10 mg/kg (Fuge & Johnson, 1986). In soils, the iodine concentration depends on sampling location and ranges between 0.5 and 20 mg/kg (Whitehead, 1984).

1.1.2 Radioactive iodine (^{129}I)

Iodine is a biophilic tracer element with forty-two isotopes and isomers at atomic numbers 108-141, including only one long-lived isotope (^{129}I , 15,7 million years), and one stable isotope, ^{127}I (Table 2). In nature iodine – 129 occurs naturally, but mainly originates from anthropogenic nuclear activities (Figure 3)

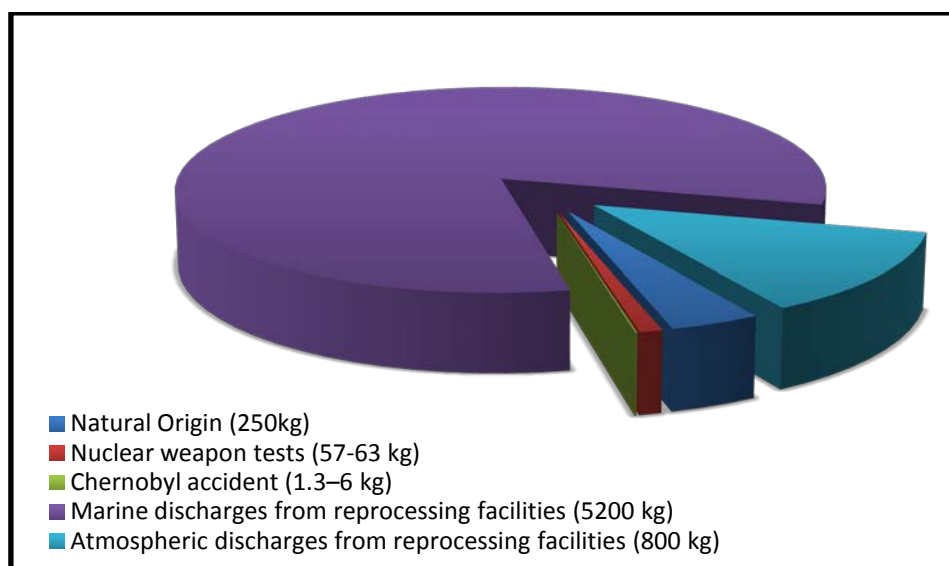


Fig.3 Sources and inventory, releases from reprocessing plants and environmental level of ^{129}I by 2007.

Marine discharge refers to the sum of discharges from La Hague and Sellafield reprocessing plants, whereas the atmospheric release refers to the sum from La Hague, Sellafield, Marcoule, WAK and Hanford. Reported marine discharges are 5200 kg and atmospheric releases of approximately 800 kg, both by 2007 (**In Paper I**).

1.1.2.1 Natural sources

Iodine-129, a beta-emitting radionuclide, is the only naturally occurring radioisotope of iodine in the environment. In the upper atmosphere I-129 is formed by cosmic-ray-induced spallation of xenon. In the earth's crust ^{129}I is produced by spontaneous fission of ^{238}U and in minor quantities by neutron bombardment of tellurium. Thermal neutron induced fission of ^{235}U is another minor natural source of ^{129}I in the lithosphere. The amount of natural ^{129}I in lithosphere is about 210 kg (10^{27} atoms) (Fabryka and Martin 1984). The reported natural isotopic ratio of $^{129}\text{I}/^{127}\text{I}$ is about 10^{-12} in terrestrial and marine environments (Fehn et al., 2007).

1.1.2.2 Anthropogenic sources

In the present environment, the source of additional ^{129}I originates mainly from anthropogenic nuclear activities such as nuclear reprocessing facilities, nuclear weapons testing and accidents associated with nuclear power plants. In a nuclear explosion, ^{129}I is mainly produced by neutron induced fission of ^{235}U and ^{239}Pu . During the period from 1945 to 1975 massive weapons production and testing programs released approximately 57-64 kg of ^{129}I to the atmosphere (Moran et al., 1999; Buraglio et al., 2000a). About 1.3–6 kg of ^{129}I entered the atmosphere from the Chernobyl accident (26 April 1986) (Aldahan et al., 2007; Michel et al., 2005). A smaller quantity of ^{129}I was released into the environment from the Fukushima accident (http://www.irs.fr/EN/news/Documents/IRSN_fukushima-radioactivity-released-assessment-EN.pdf).

On a global scale, contributions of ^{129}I from nuclear weapon tests, the Chernobyl accident and nuclear power plants are relatively insignificant (Aldahan et al., 2006; Englund, et al., 2010) compared with discharges from nuclear fuel reprocessing plants.

Discharges from nuclear reprocessing facilities into the marine and atmospheric environments represent the greatest releases (>90%) of ^{129}I (Raisbeck and Yiou, 1999; Alfimov et al., 2004; Aldahan et al., 2007; Englund, et al., 2010). Most reprocessing plants use the PUREX (plutonium uranium extraction) and/or UREX (uranium extraction) process (Uchiyama et al., 2000; Choppin & Morgenstern, 2000), where the fuel is dissolved in concentrated nitric acid (HNO_3). At low pH, most of iodine is oxidized to volatile I_2 and released from the fuel solution. Part of this iodine is trapped while a part is released to the atmosphere (Fritz and Patton, 2006). However the releases of radioactive iodine from the PUREX or the UREX processes are in the forms of different chemically reactive species (Taghipour & Evans, 2000).

Table 2 Nuclear properties of iodine isotopes.

Nuclide	Decay mode	Half life	E _{max} (keV)	Main γ -X-ray energy, keV (Abundance %)
¹⁰⁸ I	a, p	36 ms	3947 5 (100%, a)	
¹⁰⁹ I	p	100 us		
¹¹⁰ I	EC+b ⁺ , a, ep, ea	0.65 s	3444 10 (100%, a)	
¹¹¹ I	EC+b ⁺ , a	2.5 s	3152 10 (100%, a)	
¹¹² I	EC+b ⁺ , a	3.42 s	2880 30 (100%, a)	
¹¹³ I	EC+b ⁺ , ea, a	6.6 s	2610 40 (100%, a)	
¹¹⁴ I	EC+b ⁺ , ep	2.1 s		
^{114m} I	EC+b ⁺ , IT	6.2 s		
¹¹⁵ I	EC+b ⁺	1.3 m		
¹¹⁶ I	EC+b ⁺	2.91 s		
^{116m} I		3.27 us		
¹¹⁷ I	EC+b ⁺	7m	3322.1 (68%,b ⁺),4344.1 (16%, EC)	160.3
¹¹⁸ I	EC+b ⁺	13.7 m	605.71 (78%,EC+b ⁺), 545.12 (10%,EC+b ⁺)	550
^{118m} I	EC+b ⁺ , IT	8.5 m	600.71(93%,EC+b ⁺),605.71(100%,EC+b ⁺),	
¹¹⁹ I	EC+b ⁺	19.1 m	257.52 (87%,EC+b ⁺),	260, 780
¹²⁰ I	EC+b ⁺	81.0 m	0	560
^{120m} I	EC+b ⁺	53 m	0+x	
¹²¹ I	EC+b ⁺	2.12 h	0	213
¹²² I	EC+b ⁺	3.63 m	0	560
^{122m} I		80 us	0+z	
¹²³ I	EC+b ⁺	13.27 h	1074.9 (97%, EC)	159 (83%)
¹²⁴ I	EC+b ⁺	4.18 d	2557 (25%, EC), 3160 (24%, EC), 1535 (12%,b ⁺), 2138 (11%,b ⁺)	602.7 (63%), 723 (10%), 1691 (11%)
¹²⁵ I	EC	59.41 d	150.6 (100%)	35.5 (6.68%), 27.2 (40%), 27.5 (76%)
¹²⁶ I	EC+b ⁺ , b ⁻	13.11 d	869.4 (32%,b ⁻), 1489 (29%, Ec), 2155 (23%, EC)	338.6 (34%), 666.3 (33%)
¹²⁷ I		Stable		
¹²⁸ I	b ⁻ , EC+b ⁺	24.99 m	2119 (80%, b ⁻)	442.9 (17%)
¹²⁹ I	b ⁻	1.57 ×10 ⁷ y	154.4 (100%)	39.6 (7.5%), 29.5 (20%), 29.8(38%)
¹³⁰ I	b ⁻	12.36 h	587(47%), 1005 (48%)	536 (99%), 668.5 (96%), 739.5 (82%)
^{130m} I	IT, b ⁻	9.0 m	39.9525	
¹³¹ I	b ⁻	8.02 d	606 (90%)	364.5 (82%)
¹³² I	b ⁻	2.30 h	738 (13%), 1182 (19%), 2136 (19%)	667.7 (99%), 772.6 (76%)
^{132m} I	IT, b ⁻	1.39 h	1483 (8.6%, b ⁻)	132mI 1.39 h IT, _- 1483 (8.6%, _-) 600 (14%), 173.7 (8.8%)
¹³³ I	b ⁻	20.8 h	1240 (83%)	529.9 (87%)
^{133m} I	IT	9 s	1634.174 17	
¹³⁴ I	b ⁻	52.5 m	1307 (30%)	847 (95%), 884 (65%)
^{134m} I	IT, b ⁻	3.60 m	316.49 22	
¹³⁵ I	b ⁻	6.57 h	970 (22%), 1388 (24%)	1260 (29%)
¹³⁶ I	b ⁻	83.4 s	0	
^{136m} I	b ⁻	46.9 s	6.4E2 11	
¹³⁷ I	b ⁻ , b ⁻ n	24.5 s	0	
¹³⁸ I	b ⁻ , b ⁻ n	6.49 s	0	
¹³⁹ I	b ⁻ , b ⁻ n	2.29 s	0	
¹⁴⁰ I	b ⁻ , b ⁻ n	0.86 s	0	
¹⁴¹ I	b ⁻ , b ⁻ n	0.43 s	0	

d: day, EC: electron capture, b⁺: positron emission, a: alpha

Up to 2007, respectively 3800 and 1400 kg of ^{129}I have been discharged into the English Channel from the La Hague reprocessing plant and to the Irish Sea from the Sellafield reprocessing plant (**in Paper I**). During this time period, atmospheric releases from these plants have been 75 and 180 kg, respectively (**in Paper I**).

In addition to these main reprocessing facilities in France and England, there are several reprocessing facilities worldwide. The reprocessing plant located at Marcoule (France) has released approximately 145 kg of ^{129}I to the atmosphere and 45 kg to the Rhone River (**in Paper I**).

Hanford reprocessing plant (USA) released about 260 kg ^{129}I during its operation (1944–1972) and about 14 kg during its resumed operation (1983–1988) mainly to the atmosphere (Jaquish and Price, 1988; Fritz and Patton, 2006). By 2005 about 1.0 kg ^{129}I has been released from the reprocessing plant at Tokai, Japan (Shinohara, 2004). During its operation (1971–1987) Karlsruhe reprocessing plant (WAK, Germany) has released about 1.1 kg of ^{129}I to the atmosphere (Robens and Aumann, 1988). Unknown amounts of ^{129}I from reprocessing plants in Russia, China and India have also been released to environment (**in Paper I**).

1.2 Measurement of ^{129}I and ^{127}I

Radiometric analytical methods, such as gamma and X-ray spectrometry, liquid scintillation counting (LSC) and neutron activation analysis (NAA) have been used to measure iodine-129 in environmental samples.

Isotopic analytical techniques such as accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICP-MS) are known to constitute alternatives to radiometric methods for the determination of ^{129}I in environmental samples.

Gamma and X-ray spectrometry Gamma spectrometry has been used to measure high levels of ^{129}I in thyroid, urine, seaweed, and nuclear waste (Suarez et al., 1996). During the radioactive decay of ^{129}I to ^{129}Xe , the iodine-129 emits β -particles with a maximum energy of 154.4 keV, as well as 39.6 keV γ -rays and 29-30 keV X-rays. This method is based on measurement of the γ and X-rays emitted during the radioactive decay of ^{129}I , using planar high – purity germanium or silicon (Si(Li) detectors. The potential of this technique is rather limited due to radionuclide interferences, the low counting efficiency of gamma detectors, low γ - ray abundance yield (7.5%), self-shielding phenomena which are critical at the low energy levels of X- γ rays (< 40 keV) and long counting time due to often very low activity concentrations of ^{129}I in environmental samples. The reported detection limit of this method is 20 mBq (Suarez et al., 1996) when iodine was separated from the sample matrix as AgI. Measurements made directly on samples without pretreatment have been reported to have a detection limit of 100-200 mBq Maro et al., (1999).

Liquid scintillation counting (LSC) Using this method for measurement of ^{129}I , previously separated from the sample matrix, a better detection limit (10mBq) has been achieved (Suarez et al., 1996) when comparing with gamma and X-ray spectrometry. The counting efficiency of LSC for ^{129}I is around 60–95%, depending on the quench level. X- γ -spectrometry and LSC are suitable methods for analysis of nuclear waste and high level environmental samples ($^{129}\text{I}/^{127}\text{I}$ atom ratios higher than 10^{-6} or ^{129}I levels of several tens of mBq per sample). The above mentioned techniques are relatively cheap and easily accessible but are the least sensitive techniques mentioned here. Also, these techniques often require long counting time.

Neutron activation analysis. Determination of ^{129}I by NAA has been used since 1962 (Studier et al., 1962). Iodine were extracted from environmental samples and irradiated in a thermal neutron flux density of $4 - 5 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ (see Paper I). The concentration of ^{129}I were determined from the activation product ^{130}I which emits β -particles and γ -rays ($^{129}\text{I}(\text{n}, \text{gamma})^{130}\text{I} \xrightarrow{12.3\text{h}} ^{130}\text{Xe}$). The stable iodine can be determined through a (n,2n) reaction as $^{127}\text{I}(\text{n}, 2\text{n})^{126}\text{I}$. The low concentration of ^{129}I in environmental samples (10^{-17} to 10^{-11} gg^{-1}) and interfering nuclides such as ^{24}Na , ^{82}Br , ^{133}Cs , ^{128}Te and ^{235}U imply that post-irradiation chemical purification of the samples may be necessary. Overall there are a large number of publications that report on the use of NAA for measurement of ^{129}I in environmental samples (Hou et al., 2000, 2002, 2003; Seki et al., 1990; Muramatsu et al., 1988; Auman, 1981). For ^{129}I a detection limit of 1 μ Bq has been achieved when using this technique (**in Paper I**) while for ^{127}I , 1mg kg $^{-1}$ (Gilfedder et al., 2007a) has been reported.

Accelerator mass spectrometry (AMS). NAA and AMS are the main methods for measurement of low ^{129}I atom abundances ($^{129}\text{I}/^{127}\text{I}$ ratio of $10^{-6} \sim 10^{-10}$) and low mass concentrations of ^{129}I in environmental samples (see Paper I). Moreover AMS is the only method that can be used for measurement of ^{129}I in pre-nuclear age samples with $^{129}\text{I}/^{127}\text{I}$ atom ratios lower than $< 10^{-10}$ (Buraglio et al., 2000b). The detection limit (10^{-9} Bq or $^{129}\text{I}/^{127}\text{I}$ ratio of 10^{-13}) is set by the abundance sensitivity of the AMS. Similarly with NAA when using AMS, iodine needs to be separated from the sample matrix and prepared as a AgI precipitate before measurement. The precipitated AgI is dried and mixed with Ag or Nb powder for AMS measurement. The entire principle of measurement of ^{129}I using AMS is reported **in Paper 1**. The limited number of AMS facilities available around the world capable of analyzing ^{129}I and the relatively high cost per analysis are the main drawbacks of this method.

Inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS has been used for measurement mostly of ^{127}I but also for ^{129}I (Brown et al., 2007; Bienvenu et al., 2004). Low sensitivity, isobaric and molecular ion interferences (especially ^{129}Xe , $^{127}\text{IH}_2$, $^{89}\text{Y}^{40}\text{Ar}$, $^{115}\text{In}^{14}\text{N}$, $^{113}\text{Cd}^{16}\text{O}$) as well as memory effects are the main limitations for iodine-129 analysis by ICP-MS. Several attempts have been made in order to reduce the mass interferences and memory effects. Signals of xenon ions have been reduced significantly

using oxygen as reaction gas in a dynamic reaction cell (DRC) ICP-MS (Izmer et al., 2003). Using 1% of tertiary amine solution as sample matrix, memory effects are minimized (Brown et al., 2007). Due to the poor detection limit for $^{129}\text{I}/^{127}\text{I}$ of 10^{-7} , even when using DRC ICP-MS, this technique is only suitable for measurement of high level ^{129}I environmental samples (Izmer et al., 2003).

1.3 Chemical speciation analysis concept

In the environment an element can occur in different isotopic composition, oxidation states, and chemical forms as for example inorganic and organic compounds.

According to Templeton et al., (2000) the chemical speciation analysis of one element/isotope is defined as the separation and quantification of different chemical species of one element/isotope in a sample without altering the chemical forms of the element/isotope in question in the original sample.

The toxicity, bioavailability, mobility and fate of different elements/radioactive isotopes depend primarily on the chemical form in which the element in question is present and to a lesser extent on its total concentration. For example, of all arsenic compounds, the most poisonous is the inorganic As (III) which is known as a carcinogenic agent (Lamble and Hill, 1996). The arsenic toxicity decreases in the order: As (III) > As (V) > MMAA (Monomethylarsonic acid) > DMAA (dimethylarsenic acid) > other arsenic-organic compounds (Lamble and Hill, 1996). Hexavalent chromium compounds are much more toxic than those of trivalent chromium (Nriagu, 1988, Katz and Salem, 1994). An illustrative example on the importance of speciation was the well known case of drinking water contamination with hexavalent chromium which occurred in the southern Californian town of Hinkley, causing a high number of cancers (http://static.ewg.org/reports/2010/chrome6/chrome6_report_2.pdf). Iodine is considered to be a key element involved in human health (iodine toxicity and deficiency disorders). Iodide and iodate, are less toxic than elemental iodine and some organically bound iodine compounds (Hou et al., 1997). The important role of iodine in the synthesis of the thyroid hormones 3,5,3'-triiodothyronine (T_3) and of 3,5,3',5'-tetraiodothyronine (T_4) or thyroxine is widely known (Glowa and Mezyk, 1998). These hormones are essential for normal growth and physical as well as mental development. Iodine deficiency gives rise to hypothyroidism, symptoms of which are extreme fatigue, goiter, mental slowing, depression, weight gain, and low basal body temperatures. Iodine deficiency is also the main cause of preventable mental retardation, primarily occurring when babies or small children are rendered hypothyroidism by a lack of the element. Iodine toxicity can result from an intake of 2.0 mg of iodide per day. Exposure to excessive iodine levels may occur through consumption of foods and or dietary supplements. The thyroid gland enlarges as a consequence, and goiter is produced. This enlargement is also called hyperthyroidism. In addition to goiter, iodine toxicity produces ulcers on the skin. This condition has been called "kelp acne," since it can also arise from eating kelp, an ocean plant, which contains high levels of iodine.

The bioavailability of radioactive pollutants is generally related to its speciation and accordingly, chemical species of radionuclides can be a determining factor affecting their environmental impact and hazard (Andersson et al., 2009).

In the environment, iodine exists as many species, and it is well known that the chemical speciation of iodine plays a central role in determining its geochemistry. Investigating the environmental behaviour and the biogeochemistry of iodine is important not only for understanding the transport pathways of iodine, but also for a better modelling and prediction of the migration of radioactive iodine isotopes from nuclear facilities, uptake mechanisms and retention of various iodine species in the human body and the transfer of volatile organic greenhouse-active and ozone destroying iodine species (such as alkyl iodide) from the oceans to the atmosphere.

Due to the oceans being the major pool of iodine and the vast majority of reprocessing releases of iodine-129 has occurred to the oceans our understanding of the pathways of this isotope from oceans to man is crucial in determining the radiological impact of these releases. On the other hand, the releases themselves have provided us with a unique possibility to obtain a better understanding of iodine biogeochemistry in the environment. It has been known for a long time that iodine is concentrated in many marine organisms. However, the mechanism for assimilation and remineralization of iodine in marine organisms and the possible change in speciation during this process in different kinds of marine organisms are by no means clear. The investigation of the distribution of ^{129}I and ^{127}I and their chemical species in some marine organisms (e.g. seaweed) and seawater can give more information on mechanisms of assimilation and remineralization of iodine by marine organisms.

1.4 Overview of analytical techniques for chemical speciation analysis of iodine (^{129}I and ^{127}I) in environmental samples.

1.4.1 Speciation analysis of ^{127}I and ^{129}I in freshwater and seawater. Chemical speciation analysis of ^{127}I in freshwater and seawater samples has been done by high performance liquid chromatography coupled with cathodic stripping square wave voltammetry detection (HPLC-CSSWV) (Schwehr et al., 2005) or ICP-MS (Yang et al. 2007) where iodide, iodate and organic iodine (by subtracting the inorganic iodide and iodate from total iodine) forms were distinguished. Because of relatively low sensitivity, the methods mentioned above cannot be applied for analysis of environmental concentrations of ^{129}I . Due to the low concentrations of ^{129}I in the marine environment (10^{10} at/L in seawater), anion exchange chromatography followed by AMS (accelerator mass spectrometry) (Hou et al., 2007) or radiochemical neutron activation analysis (RNAA) (Hou et al., 1999a), has been applied for chemical speciation analysis of ^{129}I in seawater. Using the above mentioned method, ^{129}I in seawater samples was extracted and determined as inorganic iodine (iodide and iodate). The use of anion exchange methods for analysis of iodine species in water samples was first

reported by Wilkins and Stewart, (1982). The method is based on different affinities of iodide and iodate on an anion exchange resin, while iodide is quantitatively retained on the column, iodate passes through in the effluent. A drawback of common anion exchangers is that a part of the organic iodine may be retained on the column while a part of it passes through in the effluent. Some organic bound iodine thus may distribute among both the operationally defined iodide and iodate. The anion exchange method is furthermore rather time consuming.

In spite of the important role of the aquatic organic iodine in biogeochemical cycle of iodine, recent work on speciation analysis in seawater and freshwater have focused only on iodide and iodate quantification and relatively little is known about aquatic organic iodine. Some seawater volatile organic iodine-127 compounds, such as alkyl iodide have been determined by gas chromatography (Schall&Heumann, 1993). Due to the low level of iodine-129 encountered in aquatic environmental samples this method cannot be applied for determination of iodine-129 organic compounds in such samples. Photochemical decomposition (H_2O_2)/UV of aquatic organic iodine has been previously employed (Wong & Cheng, 2001; Schwehr, 2003). Photochemical decomposition (H_2O_2)/UV of dissolved organic iodine in seawater have been shown to produce iodide (Wong & Cheng, 2001). Possibly, photochemical destruction of organic matter also generates a pathway for inorganic iodine to associate to newly formed fragments of organic molecules although this remains uncertain (Wong & Cheng, 2001; Moore & Zafiriou, 1994). Although effort has been made on quantification of aquatic organic iodine-127, our knowledge on speciation of iodine as organic iodine (^{129}I and ^{127}I) is still limited and much more work is needed.

1.4.2 Speciation analysis of ^{127}I and ^{129}I in soil and sediment. Sequential extraction coupled with inductively coupled plasma mass spectrometry (ICP-MS) (Englund, et al., 2010), X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure spectra (EXAFS) (Schlegel, et al., 2006; Schulze and Bertsch, 1995; Feiters, et al., 2005; Shimamoto and Takahashi, 2008; Kodama, et al., 2006) have been used to determine stable iodine speciation in selected environmental samples. Using XANES and EXAFS techniques, the stable iodine is determined as iodide, iodate and organic matter associated iodine. Compared with stable iodine (^{127}I), the ^{129}I level in soil and sediment is often 4-12 orders of magnitude lower (**in Paper I**), which necessitates efficient extraction/enrichment and measurement techniques. The atomic spectroscopy based techniques mentioned above are not able to distinguish between isotopes, meaning that the speciation of the much more abundant ^{127}I isotope would completely dominate the observations. Sequential extraction coupled with RNAA (Radiochemical Neutron Activation Analysis) (Schmidt and Aumann, 1995) or AMS (Accelerator Mass Spectrometry) (Englund, et al., 2010) has been applied for chemical fractionation of ^{129}I in soil and sediment. The chemical fractionation methods have usually been based on the classical Tessier (1979) extraction protocol where the element in question was related to water soluble, exchangeable, carbonate, oxide, organic, and mineral associated forms. Literature

data (Englund et al., 2010; Hou et al., 2003; Schlegel et al., 2006; Sheppard and Thibault, 1992) have shown that iodine association with organic matter accounts for a large part of iodine pool in soil and sediments. Furthermore, the mobility of iodine in soil and sediments seems to be strongly dependent on the content and type of organic matter. Several authors have reported positive correlations between iodine concentration profiles and organic matter concentrations in soil (Aldahan et al., 2007; Lo'pez-Gutie'rrez et al., 2004; Gallagher et al., 2005). Among the constituents of organic matter, humic substances (humic and fulvic acids as well as humin) play a key role in determining the fate and mobility of radioiodine in soil and sediments. Muramatsu et al. (1996) found that iodine sorption was not enhanced by adding nonhumified organic substances, such as straw and glucose, to a rice paddy soil. To the best of our knowledge the specific association of ^{129}I to humic acid, fulvic acid, and humin has not been reported earlier.

1.4.3 Speciation analysis of ^{127}I and ^{129}I in seaweed. Different chromatographic techniques coupled to ICP-MS and UV (Shah et al., 2005) or chemical separation techniques coupled with NAA (Hou et al., 1997, 2000a) have been previously employed for speciation analysis of ^{127}I in seaweed. Using those methods various fractions such as water-soluble iodine, soluble organic iodine, iodide, iodate, and protein, pigment, polyphenol or polysaccharide-bound iodine were separated. Up to now no speciation analyses of ^{129}I in seaweed samples have been reported. However the speciation analysis of ^{129}I in seaweed samples can be done by using the methods mentioned above if after extraction and separation the ^{129}I associated to organic fractions are decomposed and converted to iodide, which finally is concentrated and purified by CCl_4 extraction and precipitated as AgI for AMS measurement. Combustion (Keogh et al., 2007) or alkaline digestion (Yiou et al., 1994) coupled with neutron activation analysis (Hou et al., 2000b) or AMS (Fhen et al., 2007) has been employed for the determination of the total ^{129}I in seaweed samples. Despite the significant role of marine algae in the iodine cycle in the environment and the fact that seaweed accumulates iodine from seawater at high concentrations, there is still a lack in understanding of the mechanism of iodine uptake in seaweed.

1.5 Scope of the study

The overall aim with this study was to improve and develop techniques for speciation analysis of iodine, especially I-129, and to apply these techniques on environmental samples.

- Develop a rapid on-line HPLC-ICP-MS method for the direct speciation analysis of ^{127}I in water samples.
- Develop a method for the quantification of organic iodine species in fresh water and seawater samples.
- Improvement of the method for ^{129}I and ^{127}I speciation analysis in soil and sediments samples: Extraction and fractionation of iodine organic matter in soil and sediment samples.
- Speciation analysis of iodine as iodide, iodate and total iodine in seawater samples collected from the Baltic Proper, Skagerrak and Kattegat.
- Speciation analysis of iodine (^{129}I and ^{127}I) as iodide, iodate and total iodine in fresh water samples from Denmark and Sweden by alkaline oxidation ($\text{NaOH} - \text{NaClO}$) of iodine organic species and anion exchange chromatography for separation of iodide and iodate.
- To investigate the spatial and temporal variation of ^{129}I and ^{127}I by analysis of archived *Fucus Vesiculosus* samples from Denmark

2. Analytical procedures used in this work

2.1 Experimental materials. Analytical standards were produced from solution of ^{129}I (NIST-SRM-4949c) purchased from National Institute of Standard and Technology (NIST) (Gaithersburg, MD, USA). The standard was diluted with iodine carrier and used for calibration during AMS analysis. Carrier free ^{125}I (NaI form) was purchased from Amersham Biotech (UK). Carrier iodine-127 (Woodward iodine with low iodine-129 content) purchased from MICAL Specialty Chemicals, New Jersey. All reagents including tetramethylammonium hydroxide (TMAH) solution (25%), nitric acid (HNO_3), ammonium acetate – acetic acid ($\text{NH}_4\text{Ac-HAc}$), hydroxylammonium chloride ($\text{NH}_2\text{OH HCl}$), potassium nitrate (KNO_3), trichloromethane (CHCl_3), sodium nitrite (NaNO_2), silver nitrate (AgNO_3), potassium disulfite ($\text{K}_2\text{S}_2\text{O}_5$), sodium hypochlorite (NaClO), used in the experiment were of analytical reagent grade. Bio-Rad AG1- \times 4 anion exchange resin 50–100 mesh was purchased from Bio-Rad laboratories, Richmond, CA and converted to NO_3^- form. The anion exchange resin was swelled in water and transferred to a column of $\phi 1.0 \times 20$ cm.

Table 3 Summary of sample analyzed in this study

Sample	Sample amount	Sampling area/ location	Relevant paper
IAEA-375 soil	10g	From Novozybkov, Bryansk, Russia collected in July 1990	Paper IV,
Danish soil	10g	Top 10 cm of 2mm sieved soil collected from 12 different locations in Denmark in 2003	Paper IV
Oxic marine sediment	10g	The upper 2-3 cm layer from Barents Sea, August 1994	Paper IV
Anoxic marine sediment	10g	The upper 40 cm layer from South Norway, August 1994	Paper IV
Seawater	400mL	Collected from 19 locations in the Baltic Sea, Kattegat and Skagerrak Basin in August 2006 and April 2007	Paper II, III, Unpublished results
Rain and lake water	400mL	Collected from different locations in Denmark and Sweden in 2007	Paper VI
Fresh and seawater	3-10 mL	Collected from different locations in Denmark in 2008- 2009	Unpublished results
Seaweed	0.1g	From Rømø, Klint and Bornholm from 1999-2010	Paper V

Table 3 List detailed information concerning samples used in this study.

2.2 On-line HPLC-ICP-MS method for the direct speciation analysis of ^{127}I in water samples (unpublished results). In this study all critical steps of HPLC-ICP-MS method development for analysis of iodine as iodide and iodate are summarized. Parameters such as selection of chromatographic column, mobile phase, flow rate, volume of sample injected, standard and sample preparation, stability of prepared

standards and samples, memory effect and repeatability were optimized to obtain separation between iodide and iodate in the shortest time possible. Analytical columns including Aquasil C18 (250x4.6mm, 5 μ m particle size), Hypurity C18 (250x4mm, 5 μ m particle size), Hamilton PRP-x100 and Ion PAC AS11 column (2.0 mm id \times 250 mm length, 13 μ m particle size, Dionex) with Ion PAC AG11 (2 \times 50 mm) guard column were tested. The peak shape and retention time were optimized by changing the concentration of buffers including mixture of acetonitrile-water (20:80), acetonitrile-2mM tetrabutylammonium hydroxide (15:85), and ammonium carbonate 0.03M in the mobile phase. When using reverse phase HPLC (Aquasil C18 and Hypurity C18) the iodide and iodate were not well separated.

From all above mentioned columns, Ion PAC AS11 column (2.0 mm id \times 250 mm length, 13 μ m particle sizes, Dionex) was used for the separation of iodide and iodate in water samples. An Ion PAC AG11 (2 \times 50 mm) guard column was applied to remove the particles and impurities in the load sample for improving the performance of the separation column. The detailed experimental conditions can be seen in Table 4. AS11 is a weakly basic anion exchange column, the separation of iodide and iodate on this column is based on the significantly different affinity of iodide and iodate, and the elution behaviors of iodide and iodate on the column by encountered anions, such as CO_3^{2-} .

Table 4 Experimental parameters of HPLC-ICPMS for the speciation analysis of ^{127}I in liquid

HPLC experimental conditions	
Column	Ion PAC AS11 Dionex (2.0 mm id \times 250 mm length, 13 μ m particle size), and an AG11 (2 \times 50 mm) guard column
Mobile phase	0.03 mol/L $(\text{NH}_4)_2\text{CO}_3$
Flow rate	0.50 mL min ⁻¹
Volume sample loaded	100 μ l
ICP –MS parameters	
Forward power	1.45 kW
Plasma gas flow rate	13 L min ⁻¹
Auxiliary gas flow rate	1.0 L min ⁻¹
Nebuliser gas flow rate	1.0 L min ⁻¹
Dwell time	30 ms

An auto-sampler was connected to the HPLC, which is used to load the sample to the column automatically. The mobile phase, (0.03 mol/L $(\text{NH}_4)_2\text{CO}_3$) from the HPLC column is directly injected to the plasma of the ICP-MS through the concentric nebulizer, and the iodine concentration in the eluent is then monitored on-line, measured and recorded. The standards and the analyzed samples were prepared in 0.03 mol/L $(\text{NH}_4)_2\text{CO}_3$. The seawater samples were diluted 20 times with 0.03 mol/L $(\text{NH}_4)_2\text{CO}_3$. The total concentration of iodine in each sample was measured independently by ICP-MS using external standards.

2.3 Quantification of total iodine in water samples by adsorption onto activated charcoal and DEAE 32 cellulose (unpublished results). Because of the low concentrations of organic iodine (^{129}I and ^{127}I) encountered in the marine environment, most work on speciation analysis in seawater are focused on iodide and iodate (^{129}I and ^{127}I) quantification. Although high concentrations of organic iodine has been reported in fresh water compared to seawater (Reifenhäuser and Heumann, 1990) there are no records of speciation studies carried out with a focus on quantification of organic iodine including also ^{129}I . Since the inorganic species (iodide and iodate) and the total concentration of stable iodine can be investigated/determined by HPLC – ICP-MS and ICP-MS respectively, this report deals with laboratory studies conducted to provide a method for determination of the total concentration of iodine-129 including inorganic as well as organic iodine-129 species in water samples. Following analysis of inorganic ^{129}I species (iodide and iodate) using anion exchange chromatography (see 2.7), the amount of organic iodine-129 encountered in studied water sample will be calculated by subtracting the inorganic iodine from total iodine. Since the added ^{125}I may behave differently from the already present ^{127}I , (isotopic equilibrium not reached) both isotopes were used to monitor adsorption and chemical yields. In this section adsorption of organic and inorganic iodine species onto activated charcoal or DEAE 32 cellulose followed by alkaline digestion or combustion of the solid sorbents (for removal of iodine from solid sorbents and destruction of organic iodine species) and extraction and back-extraction of iodine from previous step prior to precipitation as AgI (see 2.10) for iodine -129 measurement are discussed. The applied procedure is presented in Figure 4.

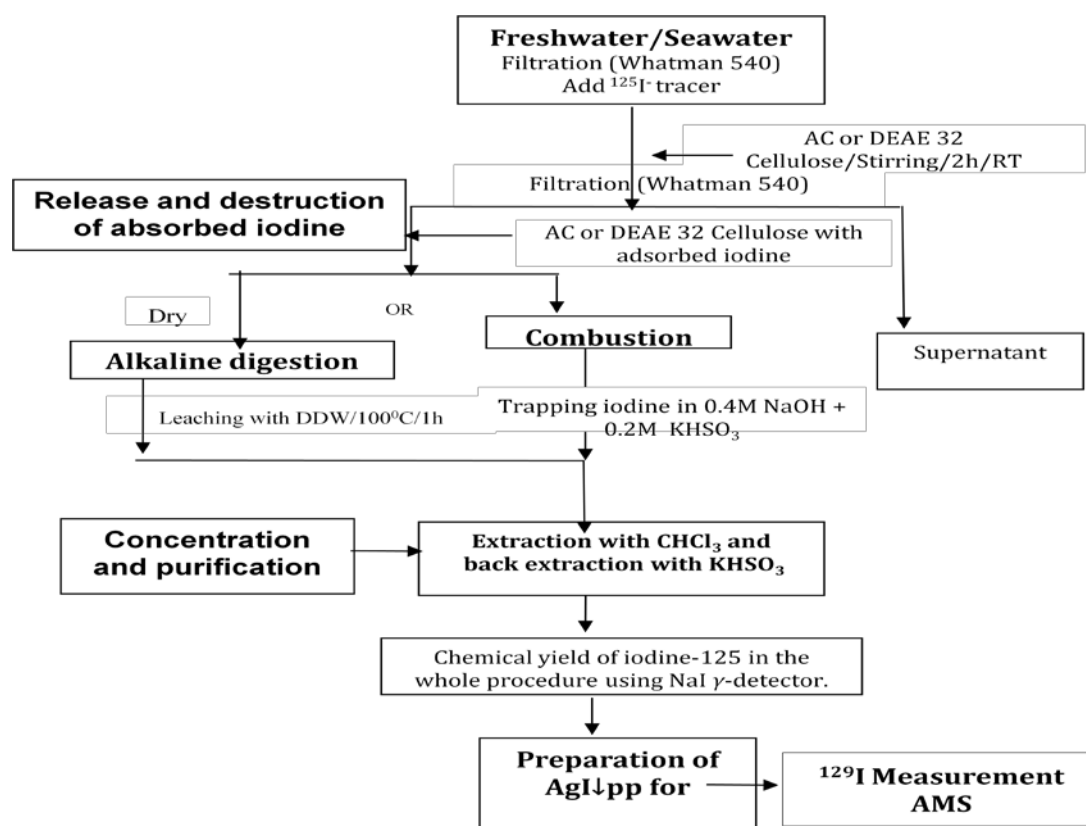


Fig. 4 Quantification of total iodine in water samples by adsorption onto activated charcoal and DEAE 32 cellulose. AC-activated carbon; RT-room temperature

In this work two potential getters were evaluated for their ability to sorb iodide, iodate and organic iodine from freshwater and seawater. These materials include activated charcoal washed with double distilled water and/or ethanol to remove fine carbon particles and DEAE 32 cellulose, an anion exchange resin widely used in protein purification/separation. The adsorption capacity of activated charcoal and DEAE 32 cellulose as a function of iodide and iodate concentrations, different pH, contact time, amount of activated charcoal and amount of DEAE 32 cellulose was investigated. A volume of 200 mL of Whatman 540 filtered water, previously analyzed for total iodine using direct injection ICP-MS, was mixed with 100 Bq of ^{125}I tracer and 5g wet activated charcoal or DEAE 32 cellulose and stirred at room temperature for 2h. The mixture was then filtered through a Whatman 540 paper filter and the concentration of total iodine in the filtrate was measured by ICP-MS. After adsorption of iodine species the activated charcoal and DEAE 32 cellulose was subjected to alkaline digestion or combustion at 900°C . For alkaline digestion the solid sorbent from the batch experiment was mixed with 5mL of 3M NaOH and the mixture was dried at $70\text{--}80^{\circ}\text{C}$, and then burnt and ashed at 350°C for 30' and 650°C for 3h, respectively.

The iodine was leached (1h) from the ashed samples with double distilled water at 100°C . The leached solution was filtered through a Whatman 540 filter and the iodine was separated from the matrix by extraction and back-extraction with CHCl_3 and KHSO_3 solution. The chemical yield of iodine-125 in the whole procedure was measured using a NaI γ -detector.

2.4 Quantification of total iodine in freshwater by $\text{K}_2\text{S}_2\text{O}_8$ oxidation of iodine organic matter (unpublished results). An alternative way of being able to include the aquatic organic bound iodine-129 fraction into total iodine concentrations would be to try and remove iodine from the organic material or try to destroy it. Assays were therefore carried out to destroy organic iodine-129 in water samples by oxidation, using $\text{K}_2\text{S}_2\text{O}_8$ or a mixture of $\text{K}_2\text{S}_2\text{O}_8/\text{NaClO}$. As previously (see 2.3) the ^{127}I was used in all conducted experiments presented in this section. The experiments were aimed at estimating the total concentration of iodine-129 in freshwater samples by destroying the organic iodine followed by reduction of all iodine species to iodide and precipitation as AgI after adding silver nitrate. The applied procedure is presented in Figure 5.

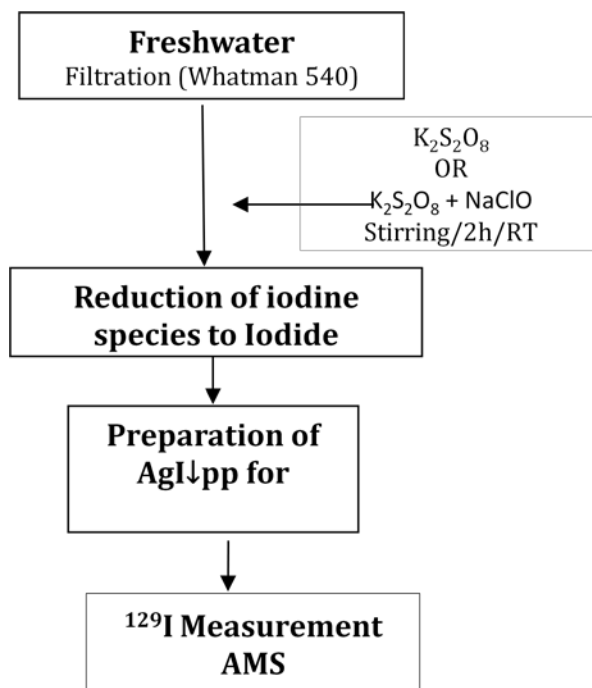


Fig. 5 Quantification of total iodine in freshwater by K₂S₂O₈ oxidation of iodine organic matter

The AgI were separated from the sample by centrifugation and the total amount of iodine-127 remaining in the supernatant was measured using ICP-MS. After determining the inorganic ¹²⁹I species (iodide and iodate) using anion exchange chromatography (see 2.7), the amount of organic iodine-129 encountered in a studied water sample will be calculated by subtracting the inorganic iodine from total iodine determined after oxidation of iodine organic matter. In the present work the efficiency of different oxidants as a function of the amount of iodine organic matter in the water sample was investigated. The total concentration of iodine in the original studied lake water sample was 9.2 ppb as determined by direct analysis of the water using ICP-MS. A volume of 200 mL of Whatman 540 filtered fresh water was mixed with 0.5g of K₂S₂O₈. Iodine associated to organic matter was supplied to the sample water by adding iodine humic substances extracted from soil (see the extraction procedure **in paper IV**) or low molecular weight organic iodine extracted from seaweed (Sash et al., 2005). The mixture was stirred for 2h at room temperature. The iodine species was then reduced to iodide by adding 1mL of 1M K₂S₂O₅ at a pH 1-2 with HNO₃. The iodide was separated from the matrix by adding 1-2mL of 1M AgNO₃ and the solution was stirred at room temperature for 30 minutes. The precipitate is separated by centrifugation at 3000 × g for 30 minutes.

2.5 A method for quantification of total iodine (organic and inorganic species) in freshwater samples by NaClO and NaOH oxidation of iodine organic species (in Paper VI). A simple method for analysis of total, (organic and inorganic species) ¹²⁹I in fresh water was developed. The method is based on oxidation of

iodide, and organic iodine to iodate. The iodate is then reduced to molecular iodine, first extracted using CHCl_3 and back-extracted in KHSO_3 solution. To a certain volume of fresh water sample (100 mL) spiked with about 50 Bq of ^{125}I tracer, 5 mL of 15% NaClO and 5 mL of 3M NaOH was added. This mixture was heat to 150°C for 3h. The iodine was separated from the matrix by extraction and back-extraction with CHCl_3 and KHSO_4 solution (see 2.9). The chemical yields of total iodine were measured by counting ^{125}I in the separated solution using a NaI γ -detector, and were found to be 44-92%. The iodine-127 and iodine -129 was measured by using ICP-MS and AMS respectively (see 2.10 and 2.11).

2.6 Chemical speciation analysis of ^{129}I and ^{127}I in soil and sediment (Paper IV). Iodine (^{127}I and ^{129}I) was sequentially extracted from soil and sediment using reagents selected to simulate changes in the pH and Eh that could occur naturally. The applied procedure is presented in Figure 6. The different forms of iodine extracted are operationally defined as water soluble, exchangeable, carbonates, oxides as well as iodine bound to humic acid, fulvic acid and to humin and minerals. Around 10 g of soil and sediment was used for the sequential extraction experiment and the leaching solutions was added in a sample/solution ratio of 10 (v/w) in each step. After extraction, the leachate was separated by centrifugation at $3000 \times g$ for 10 min. After removal of the supernatant, the remaining residue was rinsed with distilled water ($18 \text{ M}\Omega/\text{cm}$), in a water/sample ratio of 5 (v/w) by shaking the mixture for 10 minutes. The washes were combined with the leachate after centrifugation at $3000 \times g$ for 10 min. To the remaining residue and dried humic and fulvic acid fractions, 100 Bq of ^{125}I tracer was added. Iodine in these samples was then separated by combustion at a temperature of $> 800^\circ\text{C}$, using a combustion facility (Carbolite, UK). The released iodine, as I_2 , was trapped in alkali solution (0.4 M NaOH and 0.025 M $\text{K}_2\text{S}_2\text{O}_5$). The detailed experimental conditions can be seen in **Paper IV**.

2.7 Chemical speciation analysis of ^{129}I and ^{127}I (as iodide and iodate) in freshwater and seawater (see paper III and VI). For freshwater and seawater analysis, a modified version of the analytical method of Hou et al. (2007) was used for the separation of iodide and iodate. The modification made is to replace 150 mL of 2M KNO_3 with 40 mL of 10% NaClO used for elution of iodide from anion exchange column. A certain volume of sample (100-300 mL) spiked with about 50 Bq of ^{125}I tracer was loaded onto the Bio-Rad AG1- $\times 4$ (50–100 mesh) strongly basic anion exchange resin, converted to NO_3^- form at a flow rate of 1 ml min^{-1} . The column was washed with 30 mL of distilled water to wash out salts, and then with 50 mL of 0.2 M KNO_3 to wash out remaining iodate. The effluent and the washes were combined for the determination of iodate. Iodide on the column was eluted using 40 mL of 10% NaClO and saved for further purification. After taking an aliquot from iodide and iodate fraction for iodine-127 measurement (see 2.11), the iodide and iodate are extracted and back-extracted in KHSO_3 solution (see 2.9). The chemical yields of iodide and

iodate were measured by counting ^{125}I in the separated solution using a NaI γ -detector. The iodine-129 was measured by using AMS (see 2.10). This method however suffers from artefacts when the concentrations of organic iodine forms (such as alkyl iodide) are present at significant levels and should preferably not be used during such conditions. In this case the iodate fraction is overestimated because the organic iodine (such as alkyl iodide) passes through the column in the effluent with IO_3^- and is extracted and back-extracted in KHSO_3 solution (see 2.9) together with IO_3^- . When organic iodine (such as iodine associated humic substances) occur in the water samples (mostly in fresh water samples), a part of it remains on the anion exchange column while a part of it passes through the column in the effluent (iodate fraction). However the iodine associated humic substances cannot be extracted in CHCl_3 or back-extracted in KHSO_3 solution (unpublished results of present PhD study).

2.8 Analysis of ^{129}I and ^{127}I concentration in seaweed samples (in Paper V). Dried seaweed sample was ground and homogenized. Around 0.1 g of sample was taken and mixed with 5mL of 3M NaOH solution in a crucible and about 100 Bq of ^{125}I solution was added for chemical yield measurement. This mixture was dried at 70–80 $^\circ\text{C}$, burned and ashed at 350 $^\circ\text{C}$ for 30' and 650 $^\circ\text{C}$ for 3h, respectively. The iodine was leached from the ashed samples with double distilled water at 100 $^\circ\text{C}$, filtered and separated from the matrix by extraction with CCl_4 and back-extracted using a KHSO_4 solution (see 2.9). The chemical yield of iodine in the whole procedure, measured by ^{125}I tracer, ranged from 56% to 70%. The iodine-127 and iodine -129 was measured by using ICP-MS and AMS respectively (see 2.10 and 2.11).

2.9 Extraction of iodine from leached seaweed, soil, sediment and iodide and iodate separated fraction from anion exchange column method of water samples (Papers II-VI). After taking a sample aliquot for the determination of ^{127}I , 50-100 Bq of ^{125}I as a chemical yield tracer was added to all the fractions from soil/sediment and water except the fractions where ^{125}I had already been added. Then 2.0 mg of ^{127}I carrier (prepared from Woodward iodine) were added and iodate was converted to iodide using 0.5 mL of 1.0 M KHSO_3 . The solution was acidified to pH 2 with 3M HNO_3 , and the iodine was extracted using CHCl_3 after addition of NaNO_2 to oxidize iodide to I_2 . The extraction was repeated and the CHCl_3 phases were combined. The iodine in the CHCl_3 was back-extracted in KHSO_3 solution. The extraction and back extraction was repeated to purify iodine.

2.10 Preparation of ^{129}I for AMS measurements (in Papers II-VI). Iodine as iodide in the final back extracted solution was transferred to a centrifuge tube, and 1.5 mL of 3M HNO_3 was added. To the solution 1 mL of 1M AgNO_3 was added and mixed. Following centrifugation the AgI precipitate was dried at 60-70

°C, and then ground to powder. After mixing with Niobium powder, the AgI samples were pressed into a copper holder and the measurement of $^{129}\text{I}/^{127}\text{I}$ ratios was carried out using the AMS system at the Tandem Laboratory, Uppsala University (5MV Pelletron, National Electrostatic Corporation, USA) at a terminal voltage of 3.5 MV. The ^{129}I NIST-SRM 4949C standard with $^{129}\text{I}/^{127}\text{I}$ ratio of 1.1×10^{-11} was used (Alfimov 2005). Blank samples were prepared using the same procedure as for samples for total iodine, iodide and iodate. The measured $^{129}\text{I}/^{127}\text{I}$ ratio in blank samples ($1.5 \pm 0.5 \times 10^{-13}$) was two orders of magnitude lower than that in samples ($0.5\text{--}15 \times 10^{-11}$), and was subtracted from the measured value in the samples. Instrumental background for the AMS system was controlled by measurement of natural AgI (iodargyrite), which gave a $^{129}\text{I}/^{127}\text{I}$ ratio of 4×10^{-14} .

2.11 ^{127}I preparation for ICP-MS measurements. For ^{127}I determination, around 2 mL of the solutions from various fractions was diluted to 20 mL with 1% NH_3 , and Cs (as CsCl) was added as internal standard. The concentration of ^{127}I was determined using an X Series^{II} ICP MS (Thermo Electron Corporation).

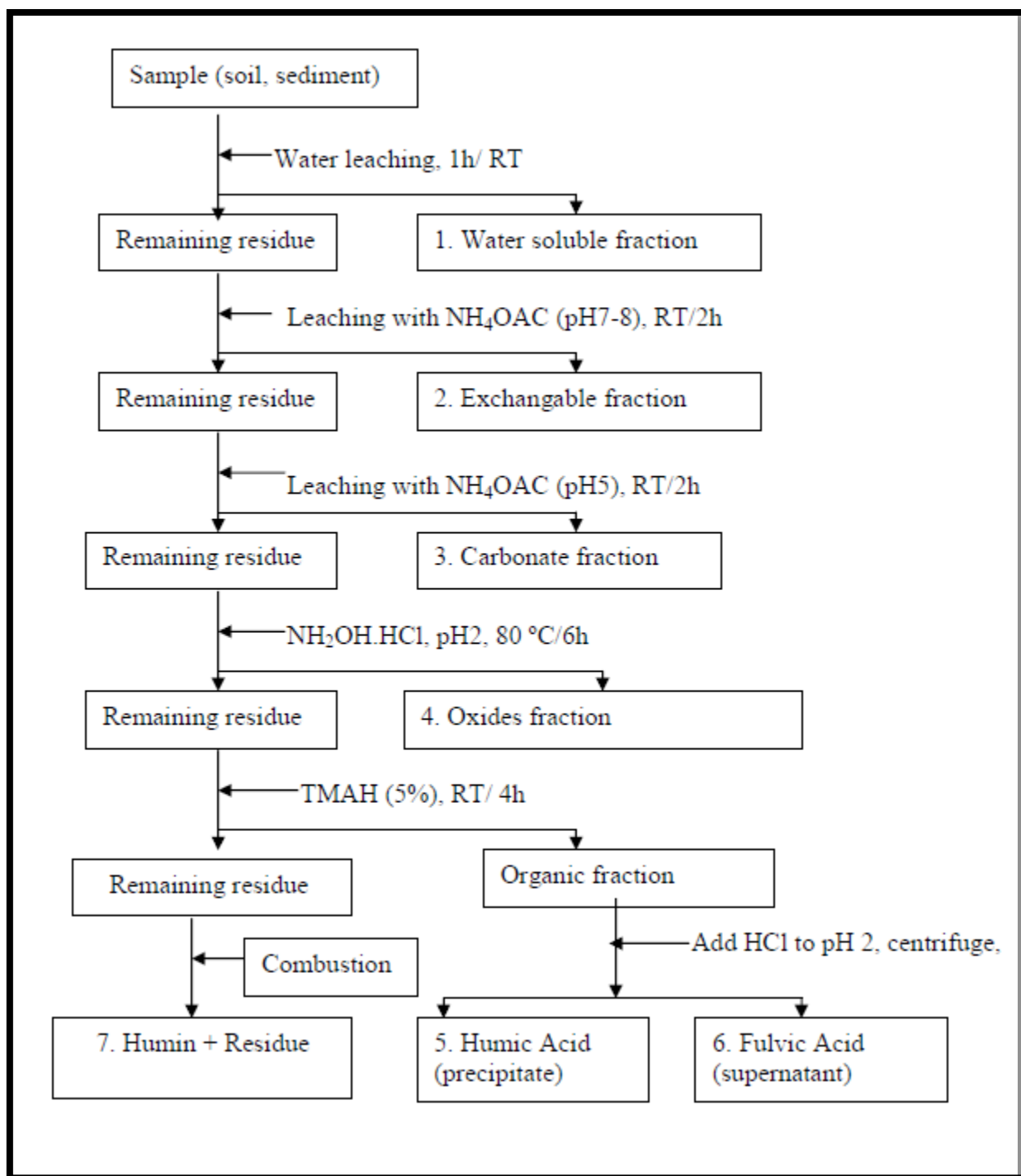


Fig. 6 Sequential extraction procedure applied for ^{129}I and ^{127}I partition in soil and sediment
TMAH- tetramethylammonium hydroxide; RT-room temperature

3. Results and Discussion

3.1 Analytical Development

3.1.1 On - line HPLC-ICP-MS method for chemical speciation analysis of ^{127}I (as iodide and iodate) in water samples (unpublished results). Previous published ion chromatography methods employed for the separation of inorganic iodine species in water samples has been associated with long analysis time, the need to use gradient elution (with 3-4 different mobile phases), required sample pre-treatment procedures, (Yamanaka et al. 1997, Liu et al. 2007, Yang et al. 2007, Chen et al. 2007, Gilfeddeer et al. 2007b) and iodate not being directly measured (Schwehr et al. 2005).

In this study complete separation (Figure 7) of iodate ($1 - t_{ret} = 0.66$ min) and iodide ($2 - t_{ret} = 4.80$ min) in water samples was accomplished when using 0.03M ammonium carbonate as mobile phase and the Ion PAC AS11 column (2.0 mm id \times 250 mm length, 13 μm particle size, Dionex) with Ion PAC AG11 (2 \times 50 mm) guard column with a flow rate of 0.5mL/min and an injection volume of 100 μL . The standards and samples were prepared in 0.03M ammonium carbonate.

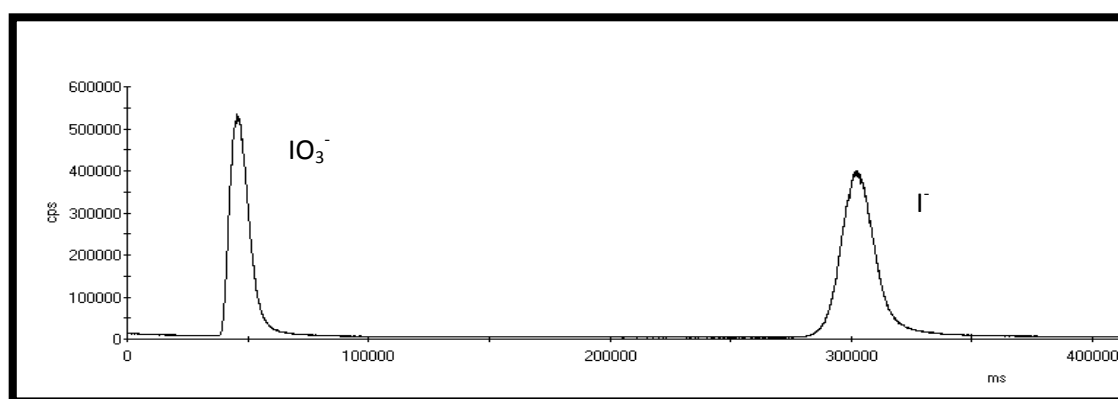


Fig. 7 HPLC-ICP-MS chromatogram for standard solution containing 20ppb of IO_3^- and 20ppb of I^- .

Absolute limits of detection for iodide and iodate calculated based on 3σ of the blank signal were found to be $0.03\mu\text{g l}^{-1}$ and $0.023\mu\text{g l}^{-1}$. Using the method developed above results in an iodide peak with significant tailing while iodate shows considerably less tailing. This is attributed to a stronger retention of iodide onto the column, also revealed by the longer elution time. A series of standard solutions were prepared using KI and KIO_3 , and measured using settings defined after optimizing, and calibration curves for iodide and iodate are shown in Figure 8.

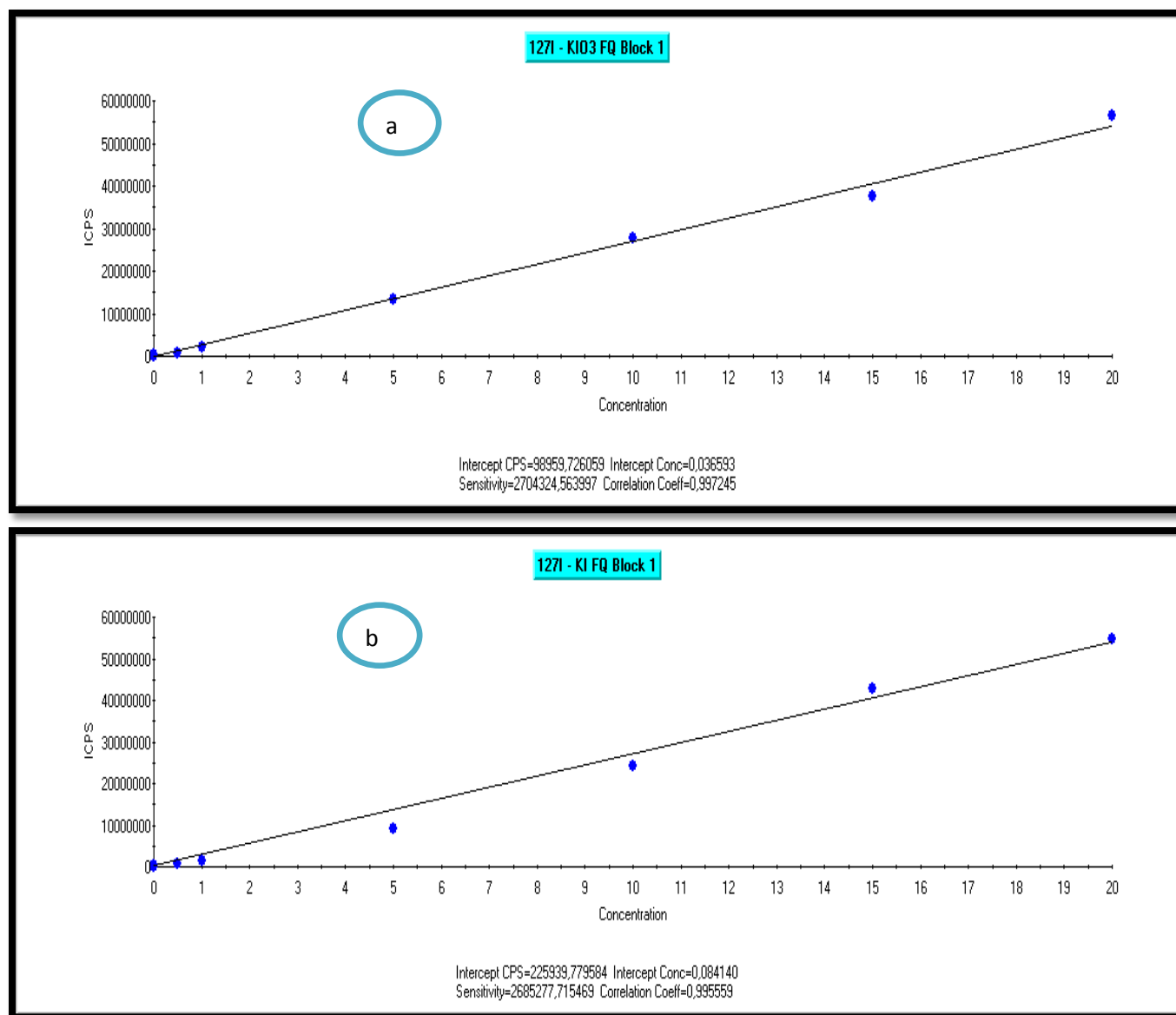


Fig. 8 Calibration curve for (a) KIO₃ and (b) KI respectively.

A good linear correlation between the prepared concentration and corresponding signal strength was observed for both iodide and iodate. By this method, no sample pretreatment is required, iodide and iodate being directly measured. The concentration of total iodine in the sample was measured using ICP-MS without the use of HPLC. By running the standard with different concentration of iodide and iodate, natural water samples with different levels of iodine and blank samples (ammonium carbonate) can be analyzed (Table 5). The analyzed seawater samples were diluted 20 times with 0.03M ammonium carbonate. No memory effects were observed when running blanks after each fifth sample. The fraction called ‘Other iodine species’ in Table 5 may constitute the fraction of organic iodine. Besides the iodide and iodate peaks in the HPLC-ICP-MS chromatogram no other peaks appeared even when the experimental time was extended to 20-30 min. Due to this, “the other iodine species” (presented in Table 5) may be expected to be retained on the column and not becoming eluted by using 0.03M ammonium carbonate, mobile phase.

Table 5 HPLC-ICPMS results of iodine species in natural water samples collected in Denmark.

Sample	Location	Sampling date	pH	Total iodine (nM)	I- (nM)	IO ₃ - (nM)	Other iodine species (nM)
Seawater	Færøerne Havvand	11-12-2008	6.5	411.1	103.78	253.54	53.78
Rain water	Ejby	03-02-2009	5	6.55	0.78	0.4	5.37
Lake	Hostrup Sø	26-01-2009	5.5	47.2	0.99	0.88	45.32
River	Suså	03-02-2009	7	74.5	1.16	4.05	70.45
Groundwater	EJ BY	27-01-2009	7	42.71	1.55	15.44	27.27

Due to the low concentrations of ^{129}I in the environment ($^{129}\text{I}/^{127}\text{I}$ is about 10^{-12} , Fehn et al., 2007; Hou et al., 2009), the above developed method cannot be applied for speciation analysis of anthropogenic iodine in environmental samples but can be applied for highly contaminated ^{129}I water samples.

3.1.2 Quantification of total iodine-129 in freshwater and seawater samples by adsorption on activated charcoal or DEAE 32 cellulose (unpublished results). Adsorption of iodine species onto activated charcoal was previously applied Woittiez et al.(1991). Several studies have been conducted in order to remove aquatic organic compound by adsorption onto activated carbon and anion exchange resin (Chen et al., 1996; Chen 1999). Activated carbon is most often involved in the purification of water. DEAE 32 cellulose, an anion exchange resin (charge independent of pH), has also been proven very useful in isolating humic material from fresh waters (Hiraide et al, 1994).

The results of the present study show that iodine from the studied lake water (with a total concentration of iodine-127 of 20 ppb) can be easily adsorbed onto 5g activated charcoal washed with double distilled water or ethanol after stirring for 2h (Table 6, experiments number 5-8 and 13-15). The sorption of iodine was not affected by the pH (Figure 9) since the fraction of ^{127}I that remains in the water phase after batch experiments (at different pH) is low. The adsorption of iodide was high over the concentration range studied (1-30 ppb) as long as the concentration of iodate was low. The presence of iodate, a relatively large ion with low effective charge, seems to block adsorption of iodide even at iodate levels as low as 5ppb (Figure 10). In order to evaluate whether or not the method would be suitable for ^{129}I analysis, iodine trapped on the sorbents must be able to be removed. Consequently, after adsorption of iodine species, the activated charcoal was subjected to alkaline digestion or combustion at 900°C followed by extraction and back-extraction of iodine with CHCl_3 and KHSO_4 solution. The chemical yield of iodine following alkaline digestion, as measured by the added ^{125}I tracer, ranged from 46% to 56%. When activated charcoal from the batch

experiment was subjected to combustion at 900⁰C (see 2.7) the chemical yield of the ¹²⁵I tracer, ranged from 66% to 70%. Compared with activated charcoal, DEAE 32 cellulose showed a slightly lower adsorption capacity of inorganic and organic iodine species (Tables 6-7).

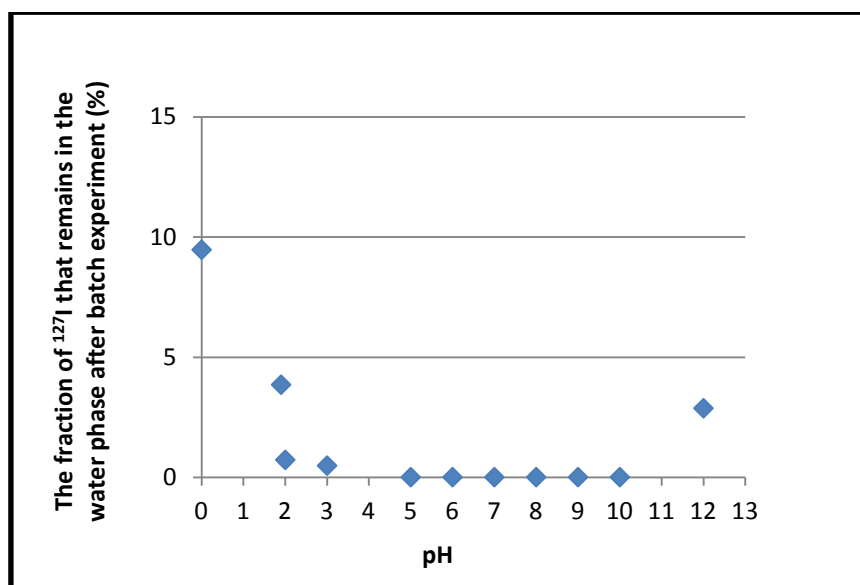


Fig. 9 Adsorption of iodine species from lake water onto activated charcoal at different pH. The concentration of iodine in lake water were 20.6ppb.

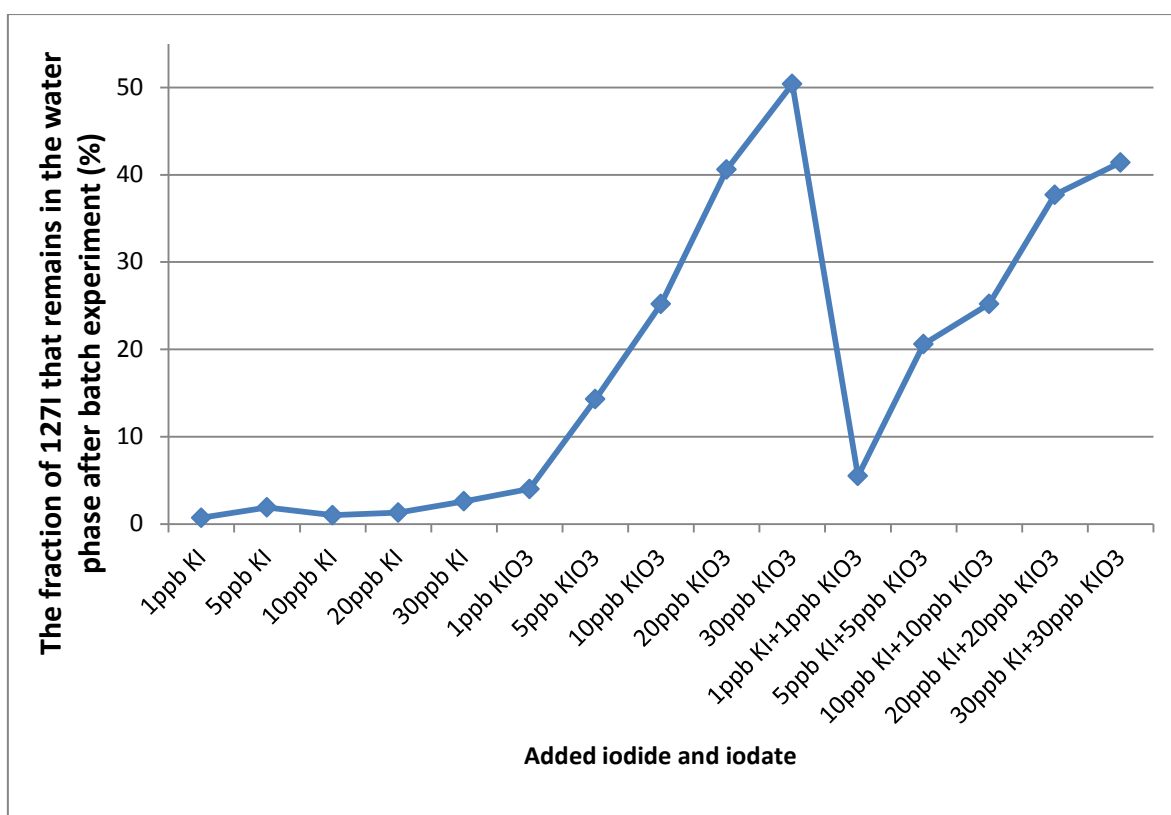


Fig. 10 Adsorption of iodine species onto activated charcoal as a function of concentrations of inorganic iodine species. The concentration of iodine in lake water was 9.2ppb.

Table 6 Adsorption of iodine species in fresh water onto activated charcoal previously washed with double distilled water and/or ethanol. The total concentration (iodide + iodate + organic iodine) in the Danish lake water used in all experiments was 20.6 ppb. The volume of water was 200ml in all experiments.

Experiment number	Adsorbant	Experiment setting	The fraction of ^{127}I that remains in the water phase after batch experiment (%)
1	AC-DDW washed	1 g AC (size 0,5-1mm) /1h Stirring/RT/filtered	10
2	AC-DDW washed	1 g AC (size 0,5-1mm) /2h Stirring/RT/ filtered	8.7
3	AC-DDW washed	1 g AC (size 0,5-1mm)/4h Stirring/RT/ filtered	7.6
4	AC-DDW washed	1 g AC (size 0,5-1mm) /8h Stirring/RT/filtered	9.6
5	AC-DDW washed	5 g AC (size 0,5-1mm) /2h Stirring/RT/ filtered	2
6	AC-DDW washed	5 g AC (size 0,5-1mm) /4h Stirring/RT/ filtered	2
7	AC-DDW washed	5 g AC (size 0,5-1mm) /8h Stirring/RT/filtered	2.6
8	AC-DDW washed	5 g AC (size 0,5-1mm) /16h Stirring/RT/filtered	5.1
9	AC-EtOH washed	1 g AC (size 0,5-1mm)/1h Stirring/RT/filtered	15
10	AC-EtOH washed	1 g AC (size 0,5-1mm)/2h Stirring/RT/ filtered	4.5
11	AC-EtOH washed	1 g AC (size 0,5-1mm) /4h Stirring/RT/ filtered	7
12	AC-EtOH washed	1 g AC (size 0,5-1mm)/ 8h Stirring/RT/ filtered	13
13	AC-EtOH washed	5 g AC (size 0,5-1mm)/1h Stirring/RT/ filtered	3.8
14	AC-EtOH washed	5 g AC (size 0,5-1mm)/4h Stirring/RT/ filtered	3
15	AC-EtOH washed	5 g AC (size 0,5-1mm)/8h Stirring/RT/ filtered	2
16	AC-EtOH washed	5 g AC (size 0,5-1mm) /16h Stirring/RT/ filtered	11.2

AC-activated charcoal; DDW-double distilled water; EtOH-ethanol; RT-room temperature

Table 7 Adsorption of iodine species onto DEAE 32 cellulose for total iodine concentration determination. The total concentration (iodide + iodate + organic iodine) in the water used in all experiments was 20.6 ppb. The volume of water was 200ml in all experiments.

Experiment number	Experiment setting	The fraction of ^{127}I that remains in the water phase after batch experiment (%)
19	1g DEAE 32 cellulose/8h Stirring/RT/ filtered	24.6
20	1g DEAE 32 cellulose/2h Stirring/RT/ filtered	24.1
21	1g DEAE 32 cellulose/4h Stirring/RT/ filtered	21.6
22	5g DEAE 32 cellulose/4h Stirring/RT/ filtered	10.1
23	5g DEAE 32 cellulose/8h Stirring/RT/ filtered	10.1
24	5g DEAE 32 cellulose/16h Stirring/RT/ filtered	15.9

RT - room temperature

Adsorption of iodine species onto activated charcoal and DEAE 32 cellulose from seawater samples shows that only 12-17% of the total iodine in seawater can be adsorbed onto those materials (Table 8). The large concentration of anions and competitive large ions that are present in the seawater are likely to block the active exchange sites and thus results in low adsorption of iodine species.

Table 8 Adsorption of iodine species onto activated charcoal and DEAE 32 cellulose from seawater. The total concentration (iodide + iodate + organic iodine) in the water used in all experiments was 35 ppb. The volume of seawater was 200ml in all experiments.

Experiment number	Adsorbant	Experiment setting	The fraction of ^{127}I that remains in the water phase after batch experiment (%)
17	AC-DDW washed	5 g AC (size 0,5-1mm)/4h Stirring/RT/filtered	83.7
18	DEAE 32 cellulose	5g DEAE 32 cellulose/4h Stirring/RT/ filtered	88.2

AC - activated charcoal; DDW - double distilled water; RT- room temperature

The results of this study reveal that the absorption of inorganic and organic iodine species onto AC or DEAE 32 cellulose has a very limited practical use during normal environmental conditions as a method for quantification of total iodine-129 in freshwater and seawater.

3.1.3 Quantification of total iodine-129 species in fresh water by $\text{K}_2\text{S}_2\text{O}_8$ oxidation of iodine organic matter (unpublished results). Persulfate oxidation of aquatic organic matter has previously been employed (Cuypers et al., 2000; Bronk et al., 2000) in order to destroy the organic matter.

The experiments performed in this study show that iodine may be released from organic matter when 200 mL of water sample is mixed with $\text{K}_2\text{S}_2\text{O}_8$ to obtain an aqueous persulfate concentration of 0.01M (Table

9). The results shows that iodine present in solution was nearly quantitatively removed (around 2.5-7.6 % of the total iodine remains in the water phase after batch experiment, Table 9, experiment numbers 3 and 4) even when the concentration of natural organic iodine compounds extracted from soils and seaweed were added to the fresh water (Table 9) increase significantly. By contrast when using a mixture of $K_2S_2O_8/NaClO$ as an oxidant, relatively high (30 - 40%) amount of iodine remains in the water phase after the batch experiment (Table 10, experiments numbers 9 and 10).

Due to the low amount of iodine that remains in the water phase after the batch experiments (Table 9, experiments numbers 3-6) we conclude that the oxidation of iodine organic matter by using $K_2S_2O_8$ followed by reduction of iodine species and precipitation with silver nitrate can be a potential method for determination of total iodine in freshwater samples. Because more samples can be treated simultaneously, the method is rapid and very suitable for field use if needed.

Table 9 Main protocols for oxidation of iodine organic matter in water samples by using $K_2S_2O_8$ for quantification of total iodine. The volume of water was 200ml in all experiments. The experiments were conducted at room temperature. All forms of iodine resulted after destruction of organic iodine were converted to iodide by adding 1mL of 1M $K_2S_2O_5$ at pH 1-2 with 3M HNO_3 and finally precipitated as silver iodide by adding 1-2 mL of 1M $AgNO_3$. After 30' stirring and centrifugation at 3000 x g for 30' the silver iodide precipitate is separated from water.

Experiment number	Experiment setting	^{127}I concentration in studied sample (ppb)	The fraction of ^{127}I that remains in the water phase after batch experiment (%)
1	0.2 g $K_2S_2O_8$ /2 mL of iodine NOM extracted from seaweed with water/sample pH 6-7/2h stirring	107.2	9.8
2	0.2 g $K_2S_2O_8$ /4 mL of iodine HSs extracted from soil with 5% TMAH/sample pH 10-11/2h stirring	43.6	19.4
3	0.5 g $K_2S_2O_8$ /3 mL of iodine NOM extracted from seaweed with water/sample pH 6-7/2h stirring	100.9	2.5
4	0.5 g $K_2S_2O_8$ /3 mL of iodine HSs extracted from soil with 5% TMAH/sample pH 10-11/2h stirring	47.1	7.6
5	1 g $K_2S_2O_8$ /4 mL mL of iodine NOM extracted from seaweed with water/sample pH 6-7/2h stirring	145.1	5.1
6	1 g $K_2S_2O_8$ /4 mL of iodine HSs extracted from soil with 5% TMAH/sample pH 10-11/2h stirring	49.80	10.0
7	0.5 g $K_2S_2O_8$ /2 mL of iodine NOM extracted from seaweed with water/sample pH 6-7/17h stirring	71.4	13.8
8	1 g $K_2S_2O_8$ /2 mL of iodine NOM extracted from seaweed with water/sample pH 6-7/17h stirring	72.0	11.9

NOM – natural organic matter; HSs – humic substances; TMAH - tetramethylammonium hydroxide;

However, direct precipitation of total iodine (without oxidation of iodine organic matter) from freshwater as silver iodine was also performed (Table 10, experiments numbers 11-14). As a result, the relative amount of total iodine was determined to be 8-15% in the filtrate after the batch experiment (Table 10, experiments

numbers 11-14), which is about the same as the experiments above using 0.01M $K_2S_2O_8$ (Table 9). These findings might be attributed to the sample matrix (organic matter), which may partially precipitate when adding silver nitrate, and thus the iodide, iodate and organic iodine were precipitated together. As long as large molecular weight humic molecules are the main carrier of organic iodine species direct co-precipitation without previous oxidation of the sample may thus be an alternative method. In fresh water highly enriched in organic matter (e.g. Humic substances) the increased ion strength due to the addition of the chemicals used induce a visible coagulation and co-precipitation of organic matter.

Table 10 Main protocols for oxidation of iodine organic matter in water samples for quantification of total iodine. The volume of water was 200ml in all experiments. The experiments were conducted at room temperature.

Experiment number	Oxidant	Experiment setting	^{127}I concentration in original sample (ppb)	The fraction of ^{127}I that remains in the water phase after batch experiment (%)
9	$K_2S_2O_8$ and NaClO	0.5 g $K_2S_2O_8$ /5 mL of 15% NaClO/3 mL of iodine NOM extracted from seaweed with water/2h stirring /1mL of 1M $K_2S_2O_5$ /pH 1-2 with HNO_3 /1-2 mL of 1M $AgNO_3$ /30' stirring/30' centrifugation at 3000 x g	105.9	39.7
10	$K_2S_2O_8$ and NaClO	0.5 g $K_2S_2O_8$ /5 mL of 15% NaClO/3 mL iodine HSs extracted from soil with 5% TMAH/sample/2h stirring /1mL of 1M $K_2S_2O_5$ /pH 1-2 with HNO_3 /1-2 mL of 1M $AgNO_3$ /30' stirring/30' centrifugation at 3000 x g	49.1	29.1
11	None	2 mL of iodine NOM extracted from seaweed with water/ pH 1-2 with HNO_3 /1-2 mL of 1M $AgNO_3$ /30' stirring/30' centrifugation at 3000 x g	254.3	8.7
12	None	2 mL of iodine HSs extracted from soil with 5% TMAH / pH 1-2 with HNO_3 /1-2 mL of 1M $AgNO_3$ /30' stirring/30' centrifugation at 3000 x g	229.3	8.4
13	None	2 mL of iodine NOM extracted from seaweed with water/ 1mL of 1M $K_2S_2O_5$ / pH 1-2 with HNO_3 /1-2 mL of 1M $AgNO_3$ /30' stirring/30' centrifugation at 3000 x g	212.2	8.7
14	None	2 mL of iodine HSs extracted from soil with 5% TMAH/ 1-2 mL of 1M $AgNO_3$ / 30' stirring /30' centrifugation at 3000 x g	211	15

NOM – natural organic matter; HSs – humic substances; TMAH - tetramethylammonium hydroxide

3.2 Analytical Development and Environmental Studies.

3.2.1 Speciation analysis as iodide, iodate and total iodine in fresh water samples by alkaline oxidation with NaOH - NaClO of organic iodine for total iodine quantification and anion exchange chromatography for separation of iodide and iodate (in paper VI). The chemical behavior of iodine and the extent with which it is able to be trapped by soils, sediments and plants or released into the atmosphere from lakes are mainly determined by its physico-chemical forms, i.e. speciation, and lesser extent by their gross concentrations. Iodine speciation analysis in lakes (as iodide, iodate and organic iodine) has not been so numerous. This report deals with laboratory studies conducted to provide needed input for determination of organic iodine as well as inorganic iodine in freshwater samples.

Conventional, organic matter destruction can be performed by hydrolysis, reduction, wet oxidation and thermal methods (Stevenson, 1994). Oxidation methods include oxidizing agents, such as potassium permanganate (KMnO_4), disodium peroxodisulphate ($\text{Na}_2\text{S}_2\text{O}_8$), or sodium hypochlorite (NaOCl). In order to be able to include iodine-129 in the total iodine budget in the lake water it is not sufficient to summarize the iodate and iodide fractions resulting from inorganic speciation analysis using standard anion exchange. Since the iodine (both ^{127}I and ^{129}I) to a large extent may be associated to organic matter it is important to destroy this fraction or at least liberate the iodine from the organic matter so that it can be included in the budget. In this study the iodine organic matter was destroyed by using NaClO in alkaline medium at 150°C for 3h and then iodine was separated from the matrix as total iodine (inorganic and organic) by extraction and back-extraction with CHCl_3 and KHSO_4 solution. The inorganic iodine (^{129}I and ^{127}I) as iodide and iodate were investigated by using anion exchange chromatography coupled with accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICP-MS) respectively. Iodine-129 concentrations in the lakes ranged from $1.3 - 12.8 \times 10^9$ at/L and show elevated concentrations in lakes located in southwest Jutland (Denmark) (Fåresø lake), near the North Sea. The concentration of stable iodine varies from 2.6 to $35.6 \mu\text{g L}^{-1}$ in Danish lakes and 4.8 to $7.6 \mu\text{g L}^{-1}$ in Swedish lakes. Except for a few locations in Denmark where organic iodine-127 accounts for around 50% of the total iodine-127 and the precipitation sample collected from Råsbäck, Sweden the iodine (both isotopes) associated to organic matter (calculated by subtracting inorganic iodine (iodide + iodate) from total iodine (see paper VI)) were not detected. Those results may be partly attributed to decomposition of NaClO which occurred while increasing the temperature (in this study 150°C for 3h). Due to this a part of iodine organic matter in those samples may not be destroyed and consequently not measured. The results further indicate that iodide (both isotopes) is the predominate speciation form in surface water of the studied lakes.

The higher concentrations of ^{129}I in lakes collected from Engesø, Fåresø and Skærsø, located near North Sea, southwest Jutland, comparing with those collected from southern Baltic Sea and Sweden (in Paper VI) may indicate that the ^{129}I concentrations in the studied lakes may be dominated by the continuous supply to the

marine environment from nuclear fuel reprocessing plants and subsequent redistribution through volatilization and precipitation.

3.2.2 Partitioning of Iodine (^{129}I and ^{127}I) Isotopes in Soil and Marine Sediments (in Paper IV).

The mobility of iodine in soil and sediments seems to be strongly dependent on the content and type of organic matter (Aldahan et al., 2007; Lo'pez-Gutie'rrez et al., 2004; Gallagher et al., 2005, Muramatsu et al., 1996). Here we present a speciation analysis method for ^{129}I and ^{127}I in soil and sediment, to identify different iodine fractions such as water soluble, exchangeable, carbonate, oxide, as well as iodine associated to humic acid, fulvic acid, humin and unaffected mineral forms. The specific association of ^{129}I to humic acid, fulvic acid, and humin has not been reported earlier. For extraction of iodine bound to organic fractions (humic and fulvic acid), two different extractants as well as optimal leaching time of this fraction were investigated (in Paper IV).

The analytical results point out that a large part of ^{127}I (30-50%) and ^{129}I (40-60%) in soil and marine sediments associate with soluble humic and fulvic acids.

The isotope distribution among organic fractions seemed to be controlled by pH conditions, where a pH value below 5.0-5.5 promoted occurrence of ^{127}I and ^{129}I in the humic acid fraction while at pH > 6 the partitioning was towards the fulvic acid fraction.

The large part (30-60%) of total iodine (^{127}I and ^{129}I) bound to the organic matter fraction as well as the primary association of both iodine isotopes with humic acid at a soil/sediment pH below 6 and with fulvic acid at a sediment pH above 6 may indicate that the mechanism by which iodine is bound to organic matter is similar for both isotopes.

Another important finding of this study is that anoxic conditions seem to increase the mobility and availability of iodine (larger fraction of extractable iodine in the water soluble and exchangeable fractions) compared to oxic, while suboxic conditions (soils) reduces the availability of water soluble fraction compared to subaqueous (marine) conditions. The distribution of $^{129}\text{I}/^{127}\text{I}$ values differed significantly between phases and samples, indicating that equilibrium with stable iodine have not yet been reached for a large fraction of the released ^{129}I . This means that geochemical models based on stable iodine behavior may not necessarily be able to predict the present behavior of I-129.

3.3 Environmental Studies.

3.3.1 Speciation analysis of iodine as iodide, iodate and total inorganic iodine in seawater profiles samples collected from the Baltic Proper, Skagerrak and Kattegat (in Papers II, III and unpublished results). Long physical half life, long residence time in the marine environment and continuous releases from nuclear fuel reprocessing plants make ^{129}I a suitable transient tracer for studies of the marine biogeochemical cycle of stable iodine, using its chemical speciation. Here we applied a modified version of

the anion exchange chromatography method of Hou et al. (2007) coupled with accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICP-MS) respectively to investigate ^{129}I and ^{127}I speciation as iodide and iodate and total inorganic iodine in seawater profile samples collected from 16 locations in August 2006 and 19 locations in April 2007 in the Baltic Proper, Skagerrak and Kattegat. Our results are in agreement with previously published data (Hou et al., 2001, Hou et al., 2002) supporting a clearly decreasing gradient of concentrations of ^{129}I from northern Kattegat to the Baltic Sea (**in Paper II**).

Previous data on surface water in the English Channel indicate ^{129}I -iodate as being the predominate species form, while in surface water of central and northern parts of the North Sea, relatively high concentrations of ^{129}I -iodide were reported (Hou et al., 2007). A similar speciation pattern is also shown by the results presented here (**in Paper III**) for the surface water samples collected from the Skagerrak-Kattegat. Through the Baltic Sea high values of $^{129}\text{I}/^{129}\text{IO}_3^-$ (2.4-30.5 in April 2007 and 2.4-99.2 in August 2006) was observed, especially in surface water (**in Paper III**). Thus, most $^{129}\text{IO}_3^-$ becomes reduced to ^{129}I as North Sea water is flowing from Kattegat through the Belt Sea and mixes with the Baltic Sea water (**In paper III**). However, this reduction may not necessarily take place in the oxygen deficient waters but may rather be due to biotic factors, taking place in the surface.

The depletion of $^{129}\text{IO}_3^-$ and enrichment of ^{129}I , in the surface water of the south Baltic Sea during the summer 2006 (algal bloom) and spring 2007 may be linked to the reduction of NO_3^- to NO_2^- by marine organism uptake. Recent literature (Campos et al., 1999; Wong, 2001) assumes that the NO_3^- and IO_3^- are taken up by marine organism in surface sea water and almost all of the IO_3^- is released as I^- . The distribution of NO_3^- concentrations in the same geographic region as was covered in this work were obtained from the WORLD OCEAN DATABASE (<http://www.nodc.noaa.gov>). These data show similar pattern of $\text{NO}_3^-/\text{NO}_2^-$ and $^{129}\text{IO}_3^-/^{129}\text{I}$ in the south Baltic Sea during the summer 2006 and spring 2007(**unpublished results**).

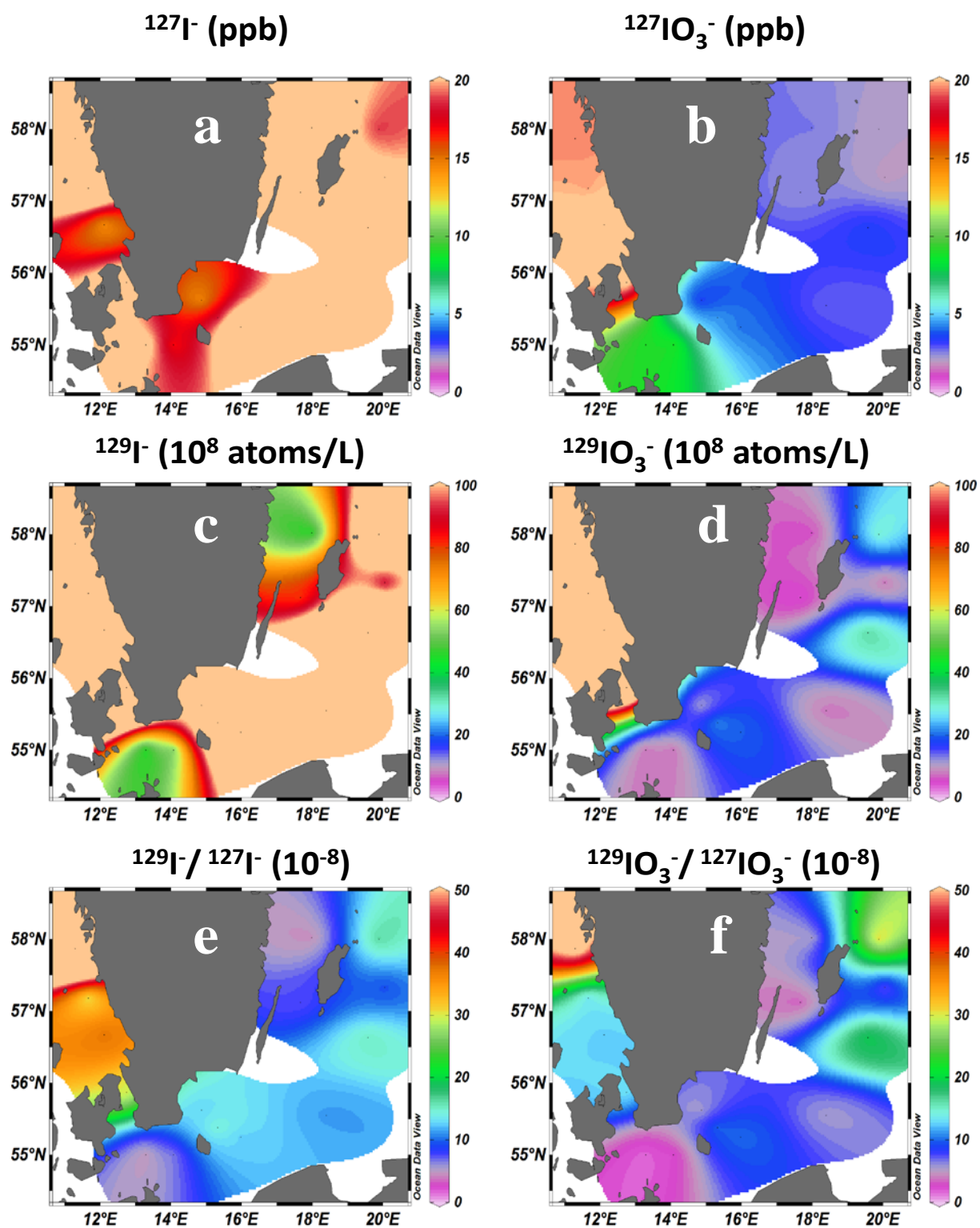


Fig. 11 Distribution of $^{127}\text{I}^-$, $^{127}\text{IO}_3^-$, $^{129}\text{I}^-$, $^{129}\text{IO}_3^-$, $^{129}\text{I}^- / ^{127}\text{I}^-$ and $^{129}\text{IO}_3^- / ^{127}\text{IO}_3^-$ (a-f) in the bottom water of Skagerrak, Kattegat and Baltic Sea for samples collected in August 2006.

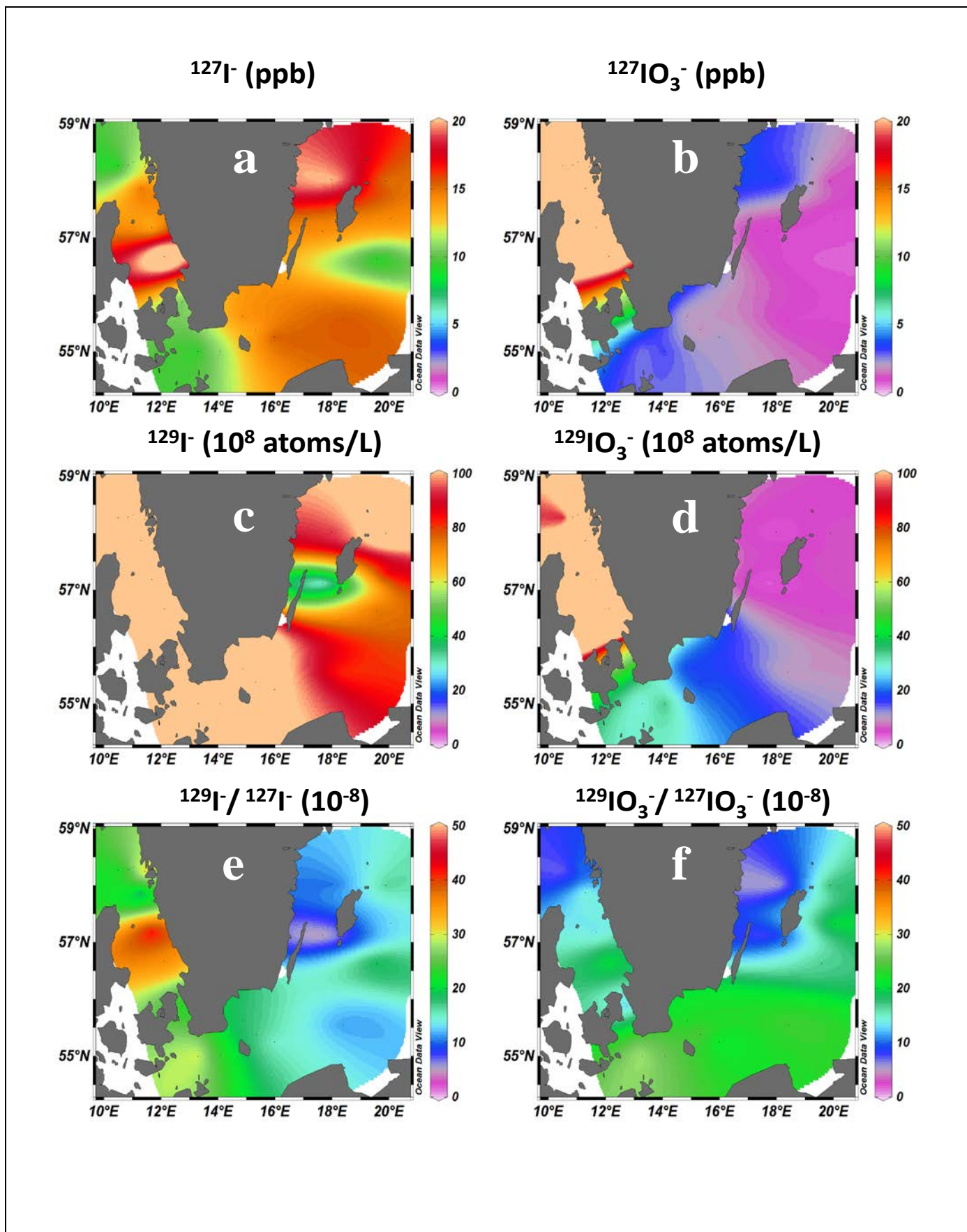


Fig. 12 Distribution of $^{127}\text{I}^-$, $^{127}\text{IO}_3^-$, $^{129}\text{I}^-$, $^{129}\text{IO}_3^-$, $^{129}\text{I}^- / ^{127}\text{I}^-$ and $^{129}\text{IO}_3^- / ^{127}\text{IO}_3^-$ (a-f) in the bottom water of Kattegat and Baltic Sea for samples collected in April 2007.

Although the oxygen concentration decreases with increasing depth in the Baltic Sea and at some locations reaches anoxic conditions (**unpublished data**), an opposite trend occurs for the concentration of $^{129}\text{IO}_3^-$ and $^{127}\text{IO}_3^-$ (Figs. 9 and 10 **and Paper III**). A possible explanation for the high concentration of $^{129}\text{IO}_3^-$ in oxygen depleted deep water of the Baltic Sea may be the transport of iodate enriched Kattegat water which flows along the bottom of the Baltic Sea and is subsequently transported to the Arkona, Bornholm and Gotland Basins. The enrichment of iodate in anoxic bottom water of the Baltic Sea may however be explained not only by the effect of saline water intrusion. Another source of iodate under such anoxic conditions can be the release of iodine as iodide and iodate from sediments by diagenetic processes (Yuita, 1992; Muramatsu et al., 1996). Our results show that the reduction of iodate in the oxygen deficient bottom water of the Baltic proper (Figs. 9 and 10) is a slow process since higher concentrations of iodate (both isotopes) was found in bottom water when comparing with surface and intermediate waters of Baltic Sea for both seasons.

The results of this work shown that (i) reduction of iodate and oxidation of iodide in Skagerrak and Kattegat may be a slow process since insignificant change in ^{129}I and ^{127}I speciation was found (ii) reduction of iodate to iodide seems to be relative fast process in surface water of the southern Baltic Sea; (iii) although suboxic or anoxic condition occur in some of the Baltic Sea deep waters, the concentration of $^{129}\text{IO}_3^-$ increases with water depth indicating that the reduction of iodate in the anoxic bottom water of Baltic Sea seems to be a slow process. The main mechanism of iodine reduction may thus be biotically driven rather than abiotic.

3.3.2 Spatial and temporal variation of ^{129}I and ^{127}I by analysis of archived *Fucus Vesiculosus* samples (in paper V). Over the past decade, liquid and gaseous release of ^{129}I from reprocessing facilities such as La Hague (France) and Sellafield (UK), has significantly increased the natural environmental concentrations by several orders of magnitude (Alfimov et al., 2004; Fehn et al., 2007; Aldahan et al., 2007). The relatively long half life of ^{129}I (15.7 myr) and the long residence time (30 kyr) of iodine in the marine environment as well as continuous releases from nuclear fuel reprocessing facilities make this isotope a suitable oceanographic tracer. Apart from marine tracer aspects we may also gain insight into the important production of volatile iodine species created by marine algae and which are released to the atmosphere. Marine algae play an important role (Leblanc et al., 2006) in the global cycle of iodine in the environment in the sense that they accumulate seawater iodine at high concentration levels and have the ability to transform a part of it into volatile organic iodine (VOI), such as methyl iodide (CH_3I) or diiodomethane (CH_2I_2 ; Carpenter et al. 2007) and release them into seawater. From the seawater surface the volatile organic iodine species are released into the atmosphere and are subsequently broken down by photolysis and reactions with ozone (O_3) (Jones & Carpenter, 2005; Martino et al. 2006) forming a reactive pool of iodine species which afterwards contribute to the ozone depletion, particle formation and cloud condensation (Küpper et al., 2008; O'Dowd et al., 2002). Despite the significant role of marine algae in the iodine cycle in the environment,

there is still a lack in understanding the mechanisms of iodine uptake in seaweed. Due to the fact that seaweed accumulate iodine from seawater at high concentrations, they are considered bioindicators or long term integrators and are included in the monitoring sampling program around many nuclear facilities. In this work we determined the concentrations of ^{129}I and ^{127}I and $^{129}\text{I}/^{127}\text{I}$ ratios in archived *Fucus Vesiculosus* samples collected from Rømø in the North Sea, Klint in the Kattegat, and Bornholm in the Baltic Sea between 2002 and 2010. The resulting data are evaluated in terms of spatial and temporal trends. In particular, we tried to address the question whether *Fucus* accumulate iodide and iodate in equal proportions. The results of this study show that the concentrations of stable iodine (^{127}I , in **Paper V**) vary from 95 ug/g dry weight to 180 ug/g dry weight for samples collected from Bornholm in the Baltic Sea, 96 ug/g dry weight to 740 ug/g dry weight for samples collected from Klint in the Kattegat and 210 ug/g dry weight to 1100 ug/g dry weight for samples collected from Rømø in the North Sea. The variation of concentration of stable iodine in seaweed samples were previously reported and were viewed as a result of different growth part of the seaweed as well as seasonal variations and different sampling locations (Hou & Yan, 1998, Hou et al., 2000b). Due to the large variations of ^{129}I and ^{127}I concentrations, the $^{129}\text{I}/^{127}\text{I}$ ratio is considered to be a more reliable index of the level of ^{129}I enrichment in seaweed (Hou et al., 2000; Keogh et al., 2007). The $^{129}\text{I}/^{127}\text{I}$ ratios are one order of magnitude higher in samples collected from Rømø in the North Sea (6.9×10^{-7} - 1.9×10^{-6}) compared with samples collected from the Baltic Sea (6.0×10^{-8} - 1.2×10^{-7}) and Kattegat (6.3×10^{-8} - 7.1×10^{-7}). These results reflect the proximity of the Rømø site to the primary release point, La Hague, and the subsequent dilution through the Jutland coastal current and further into Kattegat and the Baltic Sea. The relative decrease of seawater iodine-129 moving from the North Sea, Skagerrak towards the central parts of the Baltic Sea indicated by Hou et al., (2007) and Peng et al., (2011), Paper III seems to be partly confirmed by the iodine-129 level in *Fucus* (see **Paper V**). It is important to mention that the ratios of $^{129}\text{I}/^{127}\text{I}$ in all the samples investigated here are three – four orders of magnitude higher than the reported natural isotopic ratio of $^{129}\text{I}/^{127}\text{I}$ (10^{-12} , Fehn et al., 2007). The impact of the release of anthropogenic iodine from La Hague (France) and Sellafield (UK) reprocessing facilities is illustrated best by comparing the $^{129}\text{I}/^{127}\text{I}$ ratios in *Fucus* samples collected from all three surveys from 2002 to 2010 with the annual release of ^{129}I to the marine environments from La Hague and Sellafield (Fig 13 and results presented in Paper V). Using existing $^{129}\text{I}/^{127}\text{I}$ data in seawater from North Sea, Kattegat and Baltic Sea (Hou et al., 2007, in **Paper III**) and combining it with the $^{129}\text{I}/^{127}\text{I}$ data at corresponding years presented here, yields ratios of 0.5 for North Sea (2005), 0.7 (2006) for Southern Kattegat and 0.97 (2007) for Bornholm were found. Thus, the $^{129}\text{I}/^{127}\text{I}$ ratios in collected *Fucus* samples, closely match with corresponding data from water. The somewhat larger difference at Rømø may be an effect of this location being closer to the source and the relatively short residence time of water in the North Sea. $^{129}\text{I}/^{127}\text{I}$ ratios in water at this location may be expected to have a larger short term variance than sites further away such as Kattegat and the south Baltic Sea. The $^{129}\text{I}/^{127}\text{I}$ ratios in water at Rømø may thus deviate more from the average concentration which is reflected in the *Fucus* data. The time period over which *Fucus* is integrating water iodine is not known.

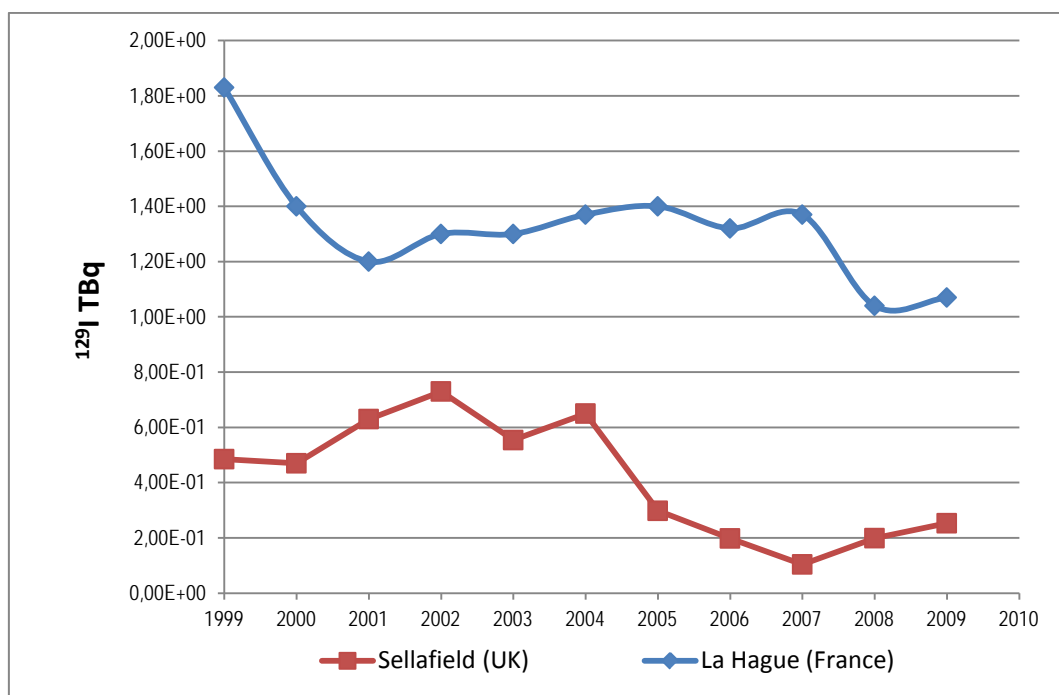


Fig. 13 Liquid Discharges of ^{129}I from La Hague (France) and Sellafield (UK) from 1999-2009. The iodine-129 data are extracted from www.ospar.org

Another factor which may influence the different in observed Fucus to seawater ratios of $^{129}\text{I}/^{127}\text{I}$ may be the different chemical speciation of the two isotopes. The Fucus plant response to uptake may differ from iodide and iodate. A difference in speciation between the isotopes will then be reflected in the Fucus $^{129}\text{I}/^{127}\text{I}$ data. Earlier publication by Hou et al., (2007) on the speciation pattern of ^{127}I and ^{129}I in surface water of the North Sea near Rømø, have shown similar concentrations of iodide-127 ($0.126 \mu\text{M}$) and iodate-127 ($0.121 \mu\text{M}$) while the concentration of iodide-129 is approximately twice as high ($14.8 \times 10^{10} \text{ at/L}$) as iodate-129 ($8 \times 10^{10} \text{ at/L}$). The results of **Paper III** show relatively high concentrations of iodide (^{127}I and ^{129}I) compared to iodate in surface water of the Kattegat basin near Klint and the Baltic Sea, Bornholm. Using the speciation pattern of iodine (^{129}I and ^{127}I) in seawater in all three surveys (Hou et al., 2007 and in **Paper III**) and comparing it with the values of $^{129}\text{I}/^{127}\text{I}$ (seaweed) relative $^{129}\text{I}/^{127}\text{I}$ (seawater) we can conclude that the iodide is somewhat more efficient to accumulate than iodate in Fucus. The high enrichment of iodine in Fucus may however be explained not only by preferential uptake of iodide since a significant increase of iodine (^{129}I and ^{127}I) in Fucus occur mostly in autumn – winter even different speciation of ^{129}I and ^{127}I in all three surveys occur. Several factors such as various physical parts of the plant, salinity, temperature, content of organic matter and nutrients concentration in seawater may also control the mechanism of iodine uptake in Fucus. However, seen from a monitoring perspective the results indicate that the Fucus Vesiculosus can be used as bio-indicator organisms for iodine-129 in this marine environment since it fairly well reflect the iodine-129 variations in water.

4. Conclusions and recommendations (perspectives)

The principal findings of this thesis are summarized as follows:

- A routine on-line HPLC-ICP-MS procedure for analysis of ^{127}I as iodide, iodate and other iodine species in fresh and seawater samples and leachate from soil/sediment and seaweed has been developed. The iodate ($1-t_{\text{ret}} = 0.66$ min) and iodide ($2-t_{\text{ret}} = 4.80$ min) were qualitatively and quantitatively measured and no sample pretreatment is required. The reproducibility and accuracy of the procedure were evaluated through standard solutions. The method is rapid and very suitable for the in situ separation on board of research vessels.
- The first documentation of ^{129}I and ^{127}I (as iodide and iodate) profiles from the Baltic Proper, Skagerrak and Kattegat covering two different seasons (summer 2006 and spring 2007) is presented. Reduction of iodate and oxidation of iodide in Skagerrak and Kattegat may be a slow process since insignificant change in ^{129}I and ^{127}I speciation was found along the water of those areas. Reduction of iodate to iodide seems to be a relatively fast process in surface water of the southern Baltic Sea since iodide is the predominant chemical specie along the surface and deep water profiles of the Baltic Sea. Furthermore in spite of suboxic or anoxic condition encountered in some of the Baltic Sea deep waters, the concentration of $^{129}\text{IO}_3^-$ increases with water depth indicating that the reduction of iodate in the anoxic bottom water of Baltic Sea as a slow process.
- Chemical speciation analysis of ^{129}I and ^{127}I (as iodide, iodate and organic iodine) in fresh water samples collected from Denmark and Sweden in 2007 was carried out. Iodine-129 concentrations in the lakes ranged from $1.3 - 12.8 \times 10^9$ at/L and show elevated concentrations in lakes located in southwest Jutland (Denmark), near the North Sea. The ^{129}I concentration in the studied lakes may be dominated by the continuous supply to the marine environment from the nuclear fuel reprocessing plants (La Hague (France) and Sellafield (U.K.)) and subsequent redistribution through volatilization from seawater followed by precipitation. Except for the Skærsø Lake, where the organic iodine – ^{127}I accounts for 50% of the total iodine, the iodide (both ^{129}I and ^{127}I) is the predominant species form in surface water of the studied lakes.

- Adsorption of iodine species on activated charcoal and or/DEAE 32 cellulose was investigated as a possibility for quantification of its total concentration (as inorganic and organic iodine) in fresh and seawater samples. The results shown that the adsorption of iodide was high over the concentration range studied (1-30ppb) as long as the concentration of iodate was low. The presence of iodate, a relatively large ion with low effective charge, seems to block adsorption of iodide even at iodate levels as low as 5ppb. Compared with activated charcoal, DEAE 32 cellulose showed a lower adsorption capacity of inorganic and organic iodine species. Adsorption of iodine species onto activated charcoal and DEAE 32 cellulose from seawater samples shows that only 9% of the total iodine in seawater can be adsorbed onto those materials. The large amounts of competitive ions that are present in the seawater may be the reasons for the low fraction of iodine absorbed onto activated charcoal and DEAE 32 cellulose. This method cannot be applied for determination of total concentration of iodine in fresh and seawater samples.
- Oxidation of organic iodine by $K_2S_2O_8$ followed by reduction to iodide and precipitation as silver iodide were studied. The results show that the iodine was quantitatively removed from studied sample, even when the concentration of iodine organic compounds extracted from soils and seaweed and added to studied fresh water increase significantly. Due to this, oxidation of iodine organic matter by using $K_2S_2O_8$ followed by reduction of iodine species and precipitation with silver nitrate can be a potential method for determination of total iodine in fresh water samples.
- Iodine-129 associated with humic and fulvic acid respectively and with humin in soil and sediments samples is reported for the first time. New findings on the partition of iodine in the organic fractions were presented. The iodine distribution among organic fractions seemed to be controlled by pH conditions, where pH value below 5.0-5.5 promoted occurrence of ^{127}I and ^{129}I in the humic acid while at $pH > 6$ the partitioning was towards fulvic acid. Another important finding of this study is that the anoxic conditions seem to increase the mobility and availability of iodine (larger fraction of extractable iodine in the water soluble and exchangeable fractions) compared to oxic, while suboxic conditions (soils) reduces the availability of water soluble fraction compared to subaqueous (marine) conditions. The distribution of $^{129}I/^{127}I$ values differed significantly between phases and samples, indicating that equilibrium with stable iodine have not yet been reached for a large fraction of the released ^{129}I . This means that geochemical models based on stable iodine behavior may not necessarily be able to predict the present behavior of I-129.

- Analyses of iodine-129 and iodine -127 time series in *Fucus Vesiculosus* collected in Denmark over the last 10 years are presented. Yields ratios of $^{129}\text{I}/^{127}\text{I}$ (seaweed) relative $^{129}\text{I}/^{127}\text{I}$ (seawater) were found to be 0.5 for North Sea (2005), 0.7 (2006) for Southern Kattegat and 0.97 (2007) for Bornholm indicating that *Fucus Vesiculosus* can be used as bio-indicator organisms for iodine-129 in marine environment since they reflect the iodine-129 in water. The results further show that the iodide is more efficient to accumulate than iodate in *Fucus*. The high enrichment of iodine in *Fucus* may however be explained not only by preferential uptake of iodide since a significant increase of ^{127}I in *Fucus* occur mostly in autumn – winter even different speciation of ^{127}I in all three investigated studies occur. Several factors such as various physical parts of the plant, salinity, temperature, content of organic matter and nutrients concentration in seawater may also control the mechanism of iodine uptake in *Fucus*. Nevertheless, the data presented here has shown that the *Fucus Vesiculosus* may accumulate preferential iodine as iodide.

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Paper I

Hou, X.L., Hansen, V., Aldahan, A., Possnert, G., Lind, O.C., Lujaniene, G. A review on speciation of iodine-129 in the environmental and biological samples. *Analytica Chimica Acta*. 2009, 632, 181-196



Review

A review on speciation of iodine-129 in the environmental and biological samples

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ARTICLE INFO

Article history:

Received 25 August 2008

Received in revised form 2 November 2008

Accepted 6 November 2008

Available online 17 November 2008

Keywords:

Iodine-129

Speciation analysis

Tracer

Bioavailability

Environmental sample

ABSTRACT

As a long-lived beta-emitting radioisotope of iodine, ^{129}I is produced both naturally and as a result of human nuclear activities. At present time, the main part of ^{129}I in the environment originates from the human nuclear activity, especially the releases from the spent nuclear fuel reprocessing plants, the $^{129}\text{I}/^{127}\text{I}$ ratios have been reached to values of 10^{-10} to 10^{-4} in the environment from 10^{-12} in the pre-nuclear era. In this article, we review the occurrence, sources, inventory, and concentration level of ^{129}I in environment and the method for speciation analysis of ^{129}I in the environment. Measurement techniques for the determination of ^{129}I are presented and compared. An overview of applications of ^{129}I speciation in various scientific disciplines such as radiation protection, waste depository, and environmental sciences is given. In addition, the bioavailability and radiation toxicity (dose to thyroid) of ^{129}I are discussed.

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Abbreviations: AMS, accelerator mass spectrometry; AmAD, activity median aerodynamic diameter; DIT, diiodotyrosine; DRC, dynamic collision/reaction cell; EXAFS, extended X-ray absorption fine structure spectra; HpGe, high purity germanium; HPLC, high performance liquid chromatography; ICP-MS, inductively coupled plasma mass spectrometry; LSC, liquid scintillation counter; MIT, monoiodothyronine; NAA, neutron activation analysis; SIMS, secondary ion mass spectrometry; T_3 , triiodothyronine; rT_3 , reverse-triiodothyronine; T_4 , thyroxine; TBAH, tetrabutylammoniumhydroxide; TEDA, triethylenediamine; TBP/OK, tri-*n*-butyl phosphate in odourless kerosene; XANES, X-ray absorption near-edge structure.

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1. Introduction

Iodine occurs as a trace element in the Earth's crust, with an average abundance of 0.45 mg kg^{-1} . Most of iodine (>70%) in the Earth's surface environment exists in the oceans with a concentration range between 45 and 60 ng mL^{-1} [1,2]. The only stable isotope of iodine is ^{127}I and the most long-lived radioisotope (15.7 My) is ^{129}I , which is also the only naturally occurring radioisotope of iodine (Table 1). Human nuclear activity has produced and released a large amount of ^{129}I to the environment thus elevating the $^{129}\text{I}/^{127}\text{I}$ ratio by at least 2 orders of magnitude compared with the natural values. Due to the long half-life and high mobility with its near conservative behavior in stored radioactive waste, ^{129}I is an important radionuclide in the waste management.

In order to assess short- and long-term consequences of radioactive contamination in the environment, information on the distribution of radionuclide species influencing mobility and biological uptake is needed [3]. Such information can be obtained by means of radionuclide speciation analysis, which can be defined as the identification and quantification of a radionuclide species in a sample. Information on total concentration (without speciation) alone is not sufficient to evaluate the potential impact of radioactive pollutants in the environment and consequently their bioavailability. Speciation analysis thus provides realistic picture about the radionuclide transport mechanisms in the environment and to the human body, as well as accurate risk assessments. Despite the significance of elemental speciation analysis, there are many difficulties associated with achieving universally accepted analytical methods as well as problems related to sampling and storage.

^{129}I is one of key radionuclides in the nuclear waste depository, ^{129}I has also been shown a very useful isotope for the age dating [4,5], a suitable oceanographic tracer for studying transport and exchange of water mass [6–15], as well as a useful environmental tracer for investigating geochemical cycle of stable iodine [16–19]. Knowledge on the speciation of ^{129}I is a key issue for safety assessment of radioactive waste repositories, for estimation of human exposure through multiple pathways, as well as its application as an environmental and oceanographic tracer. In this article, we present a review on the state-of-the-art speciation analysis methods available for ^{129}I .

Empirical data have shown different ratios of $^{129}\text{I}/^{127}\text{I}$ for the different chemical species of iodine in water, soil, sediment [20–23], implying that the speciation of anthropogenic ^{129}I in the environment is different compared with the speciation of stable iodine. The concentration of ^{129}I in the environmental samples is normally 4–12 orders of magnitude lower than that of stable iodine, for this reason the analytical methods, including the species separation and analytical techniques for the stable iodine (^{127}I) cannot be directly used for ^{129}I . The speciation of stable ^{127}I has been widely investigated in the environmental and biological samples; a few review articles related to the speciation of stable iodine are available [1,24–30]. However, the investigation of ^{129}I speciation in the environmental, especially biological samples is still very limited. To our best knowledge, a comprehensive review article on speciation of ^{129}I has not been published. This article aims to review the

occurrence, sources, environmental inventory, distribution, analytical method and speciation analysis of ^{129}I in environmental and biological samples. The bioavailability of ^{129}I and its radiation toxicity are also discussed.

2. Iodine in the nature and its speciation

Iodine is widespread trace element in the hydrosphere, lithosphere, atmosphere and biosphere. Oceans are considered the main source of iodine (concentration at $45\text{--}60 \text{ ng mL}^{-1}$) to the continental environments, which is back ventilated to the oceans by runoff at concentration of about $1\text{--}3 \text{ ng mL}^{-1}$ in fresh water. The lowest iodine concentration was observed in atmosphere ($1\text{--}100 \text{ ng m}^{-3}$ total concentration) [20,31], while the iodine concentration in precipitation ($1\text{--}6 \text{ ng mL}^{-1}$), which is removed from the atmosphere, is relatively higher [16,31]. In the continental environments, the oceanic iodine is commonly trapped by soils, sediments and biota, whereas another source of iodine is supplied by erosion of bedrock. Iodine concentration in soil ranges from 0.5 to $40 \mu\text{g g}^{-1}$ with common concentration of $1\text{--}3 \mu\text{g g}^{-1}$, and the organic soils normally has a higher iodine concentration [32,33]. Generally, sedimentary rocks, especially surface sea sediments contain comparatively high concentrations of iodine ($1\text{--}2000 \mu\text{g g}^{-1}$) compared to metamorphic and magmatic rocks ($<0.1 \mu\text{g g}^{-1}$) [2]. In the biosphere, iodine concentrations depend on its availability and concentration in the surrounding environment. High concentration of iodine was observed in seaweeds ($10\text{--}6000 \mu\text{g g}^{-1}$ dry weight), of which brown algae shows the highest values ($100\text{--}6000 \mu\text{g g}^{-1}$) [34]. Terrestrial plants normally have lower iodine concentrations ($<1 \mu\text{g g}^{-1}$) than the marine ones. In mammals, iodine is mainly concentrated to thyroid, with concentration of $0.5\text{--}5 \text{ mg g}^{-1}$ dry weight) [35,36], while iodine concentration in other tissues is normally much lower ($<1 \mu\text{g g}^{-1}$ dry weight) [37].

Iodine is an electronegative element with oxidation states of -1 , 0 , $+1$, $+3$, $+5$, and $+7$ and exists in multiform in aqueous solution. Iodine is a redox sensitive element forming a wide variety of organic and inorganic compounds and the most common inorganic forms of iodine are I^- (iodide), HOI (hypoiodous acid), I_2 (elemental iodine), and IO_3^- (iodate) in natural environmental Eh–pH conditions (Fig. 1) [38,39]. As a biophilic element, iodine occurs in many organic compounds in nature such as alkyl iodide and is incorporated in organic matters such as proteins, polyphenols and humic substances [40–43].

2.1. Speciation of iodine in water

Speciation of iodine in natural water depends on several parameters including water chemistry, pH, Eh, temperature and organic productivity. In seawater, iodine mainly exists as iodate, iodide and minor organic iodine [1]. Distribution of iodine species in seawater varies with depth and geographic location. In anoxic water, most of iodine exists as iodide, e.g. in the Baltic Sea and the Black Sea [23,44,45], while in oxygenated/oxic water, such as ocean water, the dominant species of iodine is iodate. The concentration in the ocean ranges at $<1\text{--}25 \text{ ng mL}^{-1}$ for iodide and $25\text{--}60 \text{ ng mL}^{-1}$ for iodate. Iodide maximum is often found in surface water while

Table 1

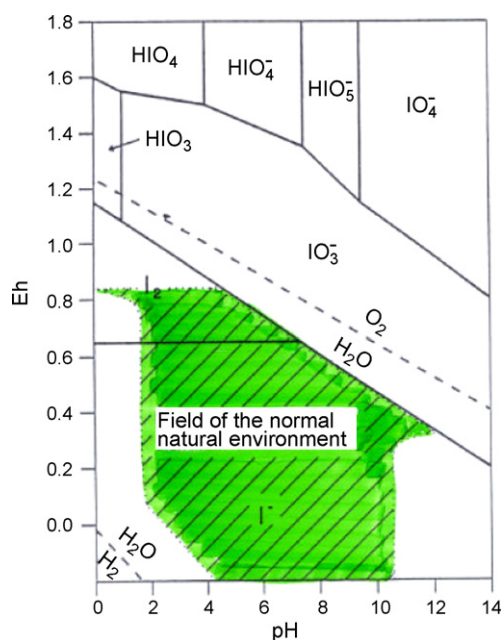
Nuclear properties and production model of iodine isotopes with half-life more than 10 min.

Isotope	Half-life	Decay mode	E_{\max} (keV)	Main γ -X-ray energy (keV) (abundance)
^{123}I	13.27 h	EC + β^+	1074.9 (97%, EC)	159 (83%)
^{124}I	4.18 d	EC + β^+	2557 (25%, EC), 3160 (24%, EC), 1535 (12%, β^+), 2138 (11%, β^+)	602.7 (63%), 723 (10%), 1691 (11%)
^{125}I	59.41 d	EC	150.6 (100%)	35.5 (6.68%), 27.2 (40%), 27.5 (76%)
^{126}I	13.11 d	EC + β^+ , β^-	869.4 (32%, β^-), 1489 (29%, EC), 2155 (23%, EC)	338.6 (34%), 666.3 (33%)
^{127}I	Stable			
^{128}I	24.99 m	β^- , EC + β^+	2119 (80%, β^-)	442.9 (17%)
^{129}I	1.57×10^7 y	β^-	154.4 (100%)	39.6 (7.5%), 29.5 (20%), 29.8(38%)
^{130}I	12.36 h	β^-	587(47%), 1005 (48%)	536 (99%), 668.5 (96%), 739.5 (82%)
^{131}I	8.02 d	β^-	606 (90%)	364.5 (82%)
^{132}I	2.30 h	β^-	738 (13%), 1182 (19%), 2136 (19%)	667.7 (99%), 772.6 (76%)
$^{132\text{m}}\text{I}$	1.39 h	IT, β^-	1483 (8.6%, β^-)	600 (14%), 173.7 (8.8%)
^{133}I	20.8 h	β^-	1240 (83%)	529.9 (87%)
^{134}I	52.5 m	β^-	1307 (30%)	847 (95%), 884 (65%)
^{135}I	6.57 h	β^-	970 (22%), 1388 (24%)	1260 (29%)

Half-lives of the isotopes are given as m: minutes; h: hours; d: days; and y: years. The decay model: EC for electron capture; β^+ for positron emission; β^- for beta emission; IT for internal transfer. An isotope may decay by more than one model.

iodide decreases to $<1 \text{ ng mL}^{-1}$ below the euphotic zone. Relatively high iodide concentration is normally found in coastal and estuary areas [15,46].

Organic iodine was reported in coastal and estuary area, corresponding to 5–40% of total dissolved iodine [47,48]. Some specific organic iodine compounds have been identified, including mainly volatile compounds, such as CH_3I , CH_2ClI , CH_2I_2 and $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ [42,43]. Although the concentration of organic iodine in seawater is low, it plays a very important role in the global geochemical cycle of iodine. The transfer of iodine from the oceans to the atmosphere, and further to the terrestrial environment, is thought to occur primarily through the emission of organic iodine hydrocarbon from the seawater [49,140]. These volatile organic iodine species were also suggested to contribute to ozone depletions in the lower stratosphere, particularly the marine boundary layer [50,51] and cloud condensation in the lower troposphere [52]. In fresh water, such as rivers, lakes and rain, iodine exists also as iodide, iodate and organic iodine, but the relative concentration of organic iodine is higher compared to seawater [53,56].

**Fig. 1.** Eh–pH diagram for iodine in water at 25 °C [38–39].

2.2. Speciation of iodine in biological and environmental samples

Iodine comprises a vital ingredient by the thyroid gland in mammals for the biosynthesis of the thyroid hormones triiodothyronine (T_3) and thyroxine (T_4). These hormones have an important influence on an extended range of biochemical reactions. Besides T_3 and T_4 , iodine also occurs as monoiodotyrosin (MIT), diiodotyrosine (DIT), and reverse-triiodothyronine (rT_3), which are mainly bound with proteins in thyroid as well as blood, but they function as free T_3 and T_4 . In addition to thyroid, iodine is also distributed in many other tissues, mainly bound with proteins [57]. In urine, iodine mainly exists as iodide, with small amount of organic iodine. The element was also found as iodide, MIT, DIT, T_4 , T_3 , rT_3 and other unknown species in fish flesh [58].

Breast milk samples taken from a selected group of European women contain $95 \pm 60 \text{ ng iodine mL}^{-1}$ milk in average. In addition, total iodine varies according to lactation state, beginning at 60 ng mL^{-1} at 2nd day (postpartum), reaching 100 ng mL^{-1} at 3rd day, and decreasing to 80 ng mL^{-1} (6th day) or 60 ng mL^{-1} constantly from 9th to 60th day. More than 80% of iodine in human milk presents as iodide, and the rest occurs as organic iodine [59–61].

In seaweed, 9–99% of iodine is water-soluble depending on the seaweed species, the highest water-soluble iodine was observed in brown algae and lowest in green algae. In the water leachate of seaweed, iodine exists mainly as iodide, the percentage of organic iodine ranges in 5–40% and the iodate is less than 5%. In biological macromolecules, iodine is mainly bound with proteins, polyphenol and pigments [42,43], and iodine in the enzymatic hydrolyzed protein exists as MIT and DIT [62]. Recently, Küpper et al. [63] directly analyzed a brown seaweed (*Laminaria digitata*) using X-ray absorption spectroscopy (iodine K-edge), and confirmed that mainly accumulated iodine exists as iodide. Their experiments also showed that iodide in seaweed readily scavenges a variety of reactive oxygen species; it is therefore proposed that the biological role of iodide in the seaweed is as an inorganic antioxidant. It was also observed that on thallus surface and in apoplast of the seaweed, iodide detoxifies both aqueous oxidants and ozone, the latter resulting in the release of high level of molecular iodine (I_2) and consequent formation of hygroscopic iodine oxides (IO_x) leading to particle formation, which are precursor to cloud condensation nuclei. Some experiments have showed a significantly increasing I_2 and particle concentrations in a culture chamber of brown seaweed, the released I_2 from the brown seaweed is therefore linked with the for-

mation of coastal new particles and cloud condensation nuclei [64–67].

2.3. Speciation of iodine in atmosphere

Total concentration of iodine in the atmosphere ranges from 1 to 100 ng m^{-3} where a high iodine concentration was observed in urban area due to the combustion of oil and coal, as well as coastal area due to emission of gaseous iodine from algae, seawater, as well as sea spray [58,63–65,68,69,165]. In the atmosphere, iodine exists as particle associated iodine (particulate iodine), inorganic gaseous iodine (I_2 , HI, HOI) and organic gaseous iodine (CHI_3 , CH_2I_2 , $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$, etc.); their concentrations vary with various parameters, such as location, season and climate [31,70–72]. Soluble species of iodine in the aerosol exist as iodide, iodate and organic iodine [54,73–75]. The photolysis of volatile gaseous iodine could generate active I which would interact with atmospheric species such as O_3 , H_xO_y , and NO_x to produce IO, HOI, ION_2 and I_2 . Production and cycling back to I could cause catalytic removal of troposphere O_3 . A mixing ratio of IO up to 6.6 ppt has been measured at Mace Head, Ireland [76]. A relative large amount of molecular iodine (I_2) may be emitted from seaweed, the released I_2 could be converted to active I, and then react with O_3 to form IO, which was supposed to be a key route to produce new particles [63].

2.4. Speciation of iodine in soil and sediment

Iodine speciation in soil and sediment is normally investigated by sequential extraction, where results showed that most of iodine in soil and sediment is associated to organic matters, mainly humic substances. Part of iodine is also adsorbed on oxides and hydroxides of iron and manganese. The fraction of soluble iodine in soil and sediment comprises minor part of soil iodine and varies with the soil chemistry [21,22,77]. Iodine in soil solution exists as iodide, iodate, and humic substance (humic acid, and fulvic acid) depending upon the soil condition. It was reported that iodate is the dominant species of iodine in soil solution under non-flooded oxidizing soil condition (85%), while under the flooded condition (anoxic) the dominant species is iodide [78].

3. Sources, inventory, and concentration level of ^{129}I in the environment

Although all ^{129}I formed in the primordial nucleosynthesis has decayed to ^{129}Xe (stable), natural processes including the reactions of high-energy particles (cosmic rays) with xenon in the upper atmosphere, spontaneous fission of ^{238}U , thermal neutron-induced fission of ^{235}U and to a lesser extent the neutron activation reactions, $^{128}\text{Te}(\text{n}, \gamma)^{129}\text{I}$ and $^{130}\text{Te}(\text{n}, 2\text{n})^{129}\text{I}$, contribute to a steady state concentration of ^{129}I . The estimated atom ratios of $^{129}\text{I}/^{127}\text{I}$ in the marine environment are 3×10^{-13} to 3×10^{-12} and even lower ratio of 10^{-15} to 10^{-14} in the lithosphere [79,80]. These ranges correspond to a steady state inventory of about 180 kg ^{129}I in the hydrosphere and about 60 kg in lithosphere (total at about 250 kg). A representative ratio of $^{129}\text{I}/^{127}\text{I}$ at 1.5×10^{-12} is commonly considered in the hydrosphere which has been based on measurement of marine sediment samples [81–83].

Since 1945, large amounts of ^{129}I have been produced and released to the environment by human nuclear activities. ^{129}I is mainly produced by neutron-induced fission of ^{235}U and ^{239}Pu in the explosion of nuclear devices, as well as in the operation of nuclear reactors for research and power production. An approximate rate of 0.17 and 0.28 g of ^{129}I per kiloton TNT equivalent is produced from fission of ^{235}U and ^{239}Pu , respectively in a nuclear

explosion. Total yield of about 540 megatons TNT equivalent was produced from nuclear weapons testing in the atmosphere or at ground level during the period from 1945 to 1975. These tests have released about 57 kg of ^{129}I to the environment [80]. The ^{129}I injected to the atmosphere, especially into the stratosphere, has a relatively long residence time, which implies mixing and fallout over a large area. A globally elevated ^{129}I level has been observed in the environment [26] resulting in a high ratio of $^{129}\text{I}/^{127}\text{I}$, particularly in the northern hemisphere. A relatively lower $^{129}\text{I}/^{127}\text{I}$ value was observed in the southern hemisphere (10^{-11} to 10^{-9}) with the lowest ratio in the equatorial regions (10^{-11} to 10^{-10}). In general, the $^{129}\text{I}/^{127}\text{I}$ ratio has been increased to 10^{-11} to 10^{-10} in the marine environment and 10^{-11} to 10^{-9} in terrestrial environment due to the nuclear weapons testing [26,35,77,84–91].

Routine operation of the nuclear reactors, for power production and research, may release ^{129}I to the environment, but no significantly increased concentration was observed in the surrounding area of nuclear power plants [14]. Records of ^{129}I releases from nuclear accidents are difficult to establish, mainly due to lack of contemporaneous measurement. The Windscale (10 October 1957) and Three Mile Island (28 March 1979) accidents may have released some amount of ^{129}I to the environment, but it was not possible to be isolated from other signals [92]. A relatively better defined ^{129}I signal is documented from the Chernobyl accident in 1986 [93]. A high ^{129}I level ($^{129}\text{I}/^{127}\text{I}$ ratio of 10^{-6}) was measured in environmental samples collected from the Chernobyl accident contaminated area [22,36,88,93–95]. A total release of ^{129}I from the Chernobyl accident was estimated to be 1.3–6 kg [93,96].

Commonly a large amount of ^{129}I is produced during the operation of a nuclear power reactor. The production efficiency of ^{129}I in the reactor depends on burn-up of the uranium fuel, which is corresponding to the power production of the reactor. It was estimated that about 7.3 mg ^{129}I is produced per MWd (megawatt day) [80]. About 9.3×10^9 MWd of nuclear power has been produced in the world from 1980 to 2005, with a production of 368 GWe in 2005 [97], it can be estimated that about 68,000 kg ^{129}I has been produced in the nuclear power reactors up to 2005. However, most of ^{129}I generated in the nuclear power production was kept in the spent fuel. The fuel elements were encased in cladding that prevented the release of gaseous radioiodine to the atmosphere, and only a small part of them was released to the environment by the reprocessing of the spent fuel.

During reprocessing of nuclear fuel (mainly by PUREX process), the fuel is first dissolved with acid (HNO_3). In this step, most of iodine is oxidized to volatile I_2 and released from the fuel solution, which may be trapped and collected, while some part may be released from the reprocessing plant to the atmosphere [98,99]. The trapped ^{129}I in solution may be stored or discharged to the environment. The ^{129}I remained in the solution is extracted into the organic solvents during following extraction process using tri-*n*-butyl phosphate (TBP), where ^{129}I may react with TBP and thus occurs in organic forms [100]. Many reprocessing plants have been operated since 1940s, and some of them are still in operation. The reprocessing plants at La Hague (France) and Sellafield (UK) are the largest. Until 2007, the La Hague reprocessing plant has discharged around 3800 kg ^{129}I to the English Channel, and the Sellafield reprocessing plant has discharged 1400 kg ^{129}I to the Irish Sea. Meanwhile these two reprocessing plants have also released 75 and 180 kg of ^{129}I to the atmosphere, respectively. Another European spent fuel reprocessing plant was located at Marcoule (France) which has also released comparable amount of ^{129}I (145 kg) to the atmosphere, but relatively small amount of liquid ^{129}I (45 kg) to the Rhone river. Annual discharges of ^{129}I from these three reprocessing plants are shown in Fig. 2 (liquid discharges) and Fig. 3 (atmosphere releases) [7,15,89,101,102]. It can be seen that a similar amount of

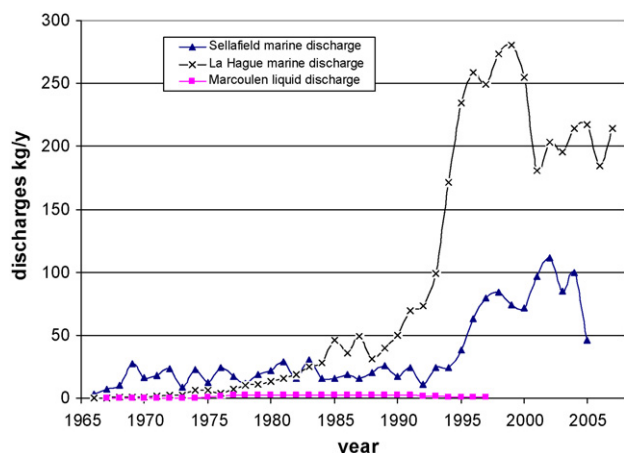


Fig. 2. Liquid discharges of ^{129}I from spent nuclear fuel reprocessing plants at La Hague (France), Marcoule (France) and Sellafield (UK) (literature refers to the text).

^{129}I has been released to the atmosphere from the three reprocessing plants with a relative constant rate of each ($2\text{--}10\text{ kg y}^{-1}$). The marine discharges of ^{129}I from La Hague and Sellafield is smaller and relatively constant before 1990 ($<50\text{ kg y}^{-1}$), later on the discharge of ^{129}I increased significantly to about 250 kg y^{-1} for La Hague and 80 kg y^{-1} for Sellafield. As a consequence, the ^{129}I concentration in the Irish Sea, English Channel, North Sea, and Nordic Seas has significantly increased and the $^{129}\text{I}/^{127}\text{I}$ ratio in these sea-water has elevated to values of 10^{-8} to 10^{-5} [6,7,11–15,23,103–108]. Even high level of ^{129}I concentration with a ratio of $^{129}\text{I}/^{127}\text{I}$ at 10^{-6} to 10^{-4} has been measured in the terrestrial samples collected near the reprocessing plants at La Hague, Marcoule and Sellafield [77,105,109]. These high ratios are attributed to local deposition of atmospheric releases of ^{129}I from the reprocessing plants. ^{129}I has also been released from other reprocessing plants mainly to atmosphere, in which Hanford reprocessing plant (USA) released about $260\text{ kg }^{129}\text{I}$ during its operation (1944–1972) [110] and about 14 kg during its resumed operation (1983–1988) [82]; reprocessing plant at Tokai, Japan released about $1.0\text{ kg }^{129}\text{I}$ since its operation from 1997 until 2005 [111,112]; about 1.1 kg of ^{129}I was released from the Karlsruhe reprocessing plant (WAK, Germany) during its operation (1971–1987) [113], and unknown amount of ^{129}I from reprocessing plants in Russia, China and India. An elevated ^{129}I levels with $^{129}\text{I}/^{127}\text{I}$ ratio of 10^{-6} to 10^{-4} have been also reported in samples col-

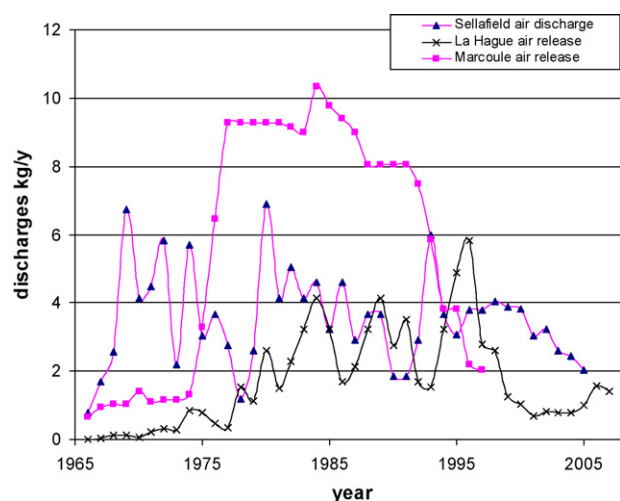


Fig. 3. Atmospheric releases of ^{129}I from spent nuclear fuel reprocessing plants at La Hague (France), Marcoule (France) and Sellafield (UK).

lected in the regions near the reprocessing plants at WAK, Germany, Hanford, USA, Tokai, Japan, and India [98,13–116].

Table 2 summarizes the sources, inventory and environmental level of ^{129}I . It is clear that presently the main source of ^{129}I is the reprocessing plants at La Hague and Sellafield. However, the major part of ^{129}I produced in reactors around the world, mainly power reactor ($>90\%$), is still stored and pending for future reprocessing. At present, the different levels of $^{129}\text{I}/^{127}\text{I}$ in the environment are envisaged as 10^{-12} for the pre-nuclear era, 10^{-9} in slightly contaminated regions and 10^{-9} to 10^{-6} in regions affected by the releases from the reprocessing plants. The highest ratio of $^{129}\text{I}/^{127}\text{I}$ at 10^{-6} to 10^{-3} was found in regions locating at the vicinity ($<50\text{ km}$) of the reprocessing plants.

4. Measurement of ^{129}I

^{129}I decays by emitting β -particle with a maximum energy of 154.4 keV and γ -ray of 39.6 keV as well as X-rays ($29\text{--}30\text{ keV}$) (Table 1). It can therefore be measured by γ -X-spectrometry and β -counting using liquid scintillation counters (LSC). Neutron activation analysis (NAA) is another radiometric method for the determination of ^{129}I . The method is based on neutron activation of ^{129}I to ^{130}I , a short-lived radionuclide, emitting high-energy γ -rays (536 keV (99%), 668.5 keV (96%), and 739.5 keV (82%)), which is easily and efficiently measured by γ -spectrometry. Mass spectrometry, such as accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICP-MS) has also been used for the determination of ^{129}I . A summary of the most common used methods is presented below.

4.1. Gamma and X-ray spectrometry

Gamma and X-ray spectrometry have been used to measure ^{129}I in thyroid, urine, seaweed, and nuclear waste by using HpGe or plenary Si detector [104–106,117,118]. This is based on the counting the $39.6\text{ keV } \gamma$ -ray or $29.46 + 29.48\text{ keV}$ (58.1%) X-rays. Due to the low counting efficiency of gamma detector ($<2\%$), low γ -ray abundance (7.5%), and high background, a detection limit of $20\text{--}200\text{ mBq}$ was obtained [104,117,118] depending on the level of interfering radionuclides. In addition, due to the low energy of X- γ rays ($29\text{--}40\text{ keV}$) and normally big sample used ($50\text{--}500\text{ g}$), elaborate self-absorption correction has to be carried out in order to obtain accurate results. A chemical separation of iodine from the matrix and interfering radionuclides can improve the detection limit to around 20 mBq when using gamma spectrometry. In addition, due to small size of the separated sample ($<20\text{ mg}$), the self-absorption correction can be neglected.

4.2. Liquid scintillation counting (LSC)

Due to high beta energy of ^{129}I (154 keV), a better counting efficiency of LSC for ^{129}I ($60\text{--}95\%$) compared with X- γ -spectrometry ($<5\%$) can be obtained depending on the quench level. In this method, iodine has to be separated from the sample matrix as well as other radionuclides before counting. A detection limit of 10 mBq has been reported [117].

4.3. Neutron activation analysis

Neutron activation analysis was firstly proposed and applied in 1962 [79,119] for the determination of ^{129}I , which based on the following nuclear reaction:

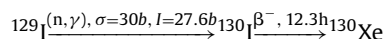


Table 2Sources, inventory/releases and environmental level of ^{129}I .

Source	Inventory/release (kg) ^a	$^{129}\text{I}/^{127}\text{I}$ ratio in the environment	Reference ^b
Nature	250	$\sim 1 \times 10^{-12}$	[81–83]
Nuclear weapons testing	57	1×10^{-11} to 1×10^{-9}	[26,35,83–89]
Chernobyl accident	1.3–6	10^{-8} to 10^{-6} (in contaminated area)	[22,36,89,94–96,127]
Marine discharge from European NFRP by 2007	5200	10^{-8} to 10^{-6} (North Sea and Nordic Sea water)	[6,7,11,13–15,23,103,104,106–108]
Atmospheric release from European NFRP by 2007	440	10^{-8} to 10^{-6} (in rain, lake and river water in west Europe)	[16,125,126,128]
		10^{-6} to 10^{-3} (in soil, grass near NFRP)	[77,105,109,113]
Atmospheric release from Hanford NFRP	275	10^{-6} to 10^{-3} (in air near NFRP)	[98,115]

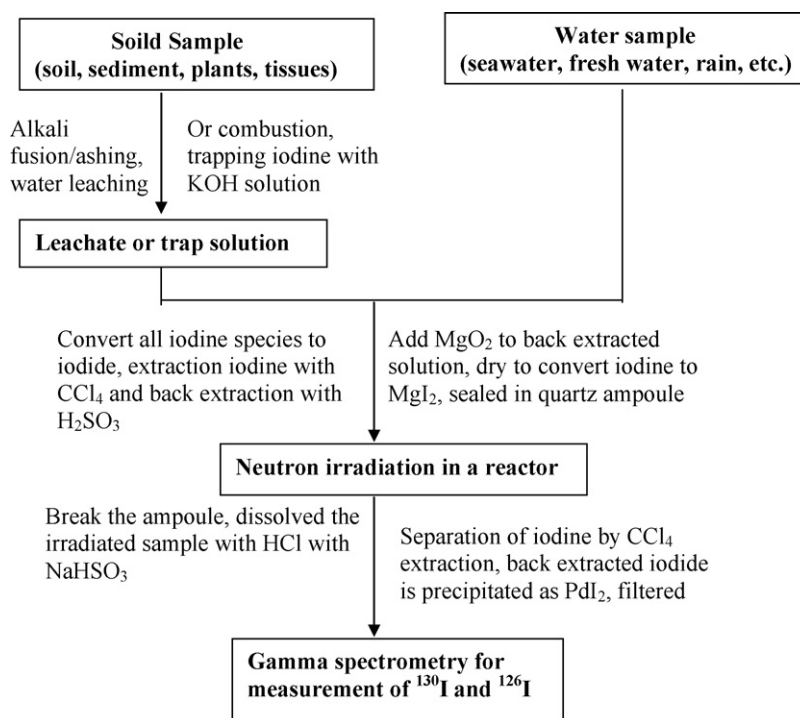
^a Marine discharge refers to the sum discharges from La Hague and Sellafield reprocessing plants; the atmospheric release from European reprocessing plant refers to a sum of those from La Hague, Sellafield, Marcoule and WAK. The source of the data refers to the literatures cited in the text.

^b The references for the environmental level of ^{129}I ; NFRP: nuclear fuel reprocessing plant.

By measurement of activation product, ^{130}I (12.3 h), decaying by emitting beta particles and gamma rays (Table 1), ^{129}I is determined. Using NAA, ^{129}I can be determined with a better sensitivity compared with the direct measurement due to the high specific radioactivity of ^{130}I and suitable gamma energies (418 keV (34%), 536.1 keV (99%), 668.5 keV (96%), and 739.5 keV (82%)). However, interfering nuclear reactions from some nuclides other than iodine isotopes may occur during production of ^{130}I in the samples. These nuclides include ^{235}U , ^{128}Te , and ^{133}Cs . Because of the extremely low concentration of ^{129}I in environmental samples (10^{-17} to $10^{-11} \text{ g g}^{-1}$), these interfering nuclides have to be removed from the sample before irradiation to avoid nuclear interference that will generate spurious results. The radioactivity produced from the activation products of the sample matrix elements, such as ^{24}Na and ^{82}Br , is more than 10 orders of magnitude higher than that of ^{130}I , which hinders the direct measurement of ^{130}I after irradiation. Bromine in particular, produces γ -rays of ^{82}Br that interferes with the measurement of ^{130}I , which necessities a post-irradiation chemical purification to provide a necessary decontamination with respect to this nuclide. Besides ^{129}I , stable iodine (^{127}I) can be simul-

taneously determined by fast neutron reaction $^{127}\text{I}(n, 2n)^{126}\text{I}$. A typical analytical procedure for the determination of ^{129}I by radiochemical NAA [120] is shown in Fig. 4.

For solid sample, such as soil, sediment, vegetations and tissues, alkali fusion/ashing method can be used for decomposition of sample, in which the sample is first mixed with alkali solution, and then ashed or fused at 600°C . Iodine is then leached from the decomposed sample using water. The experimental results have showed that the recovery of iodine in ashing or fusion procedure is higher than 80% [121]. A combustion method has also widely been used for the separation of iodine from solid samples [121,122]. In this method, sample is combusted at higher temperature ($>800^\circ\text{C}$), the released iodine, mainly as I_2 , is trapped with alkali solution (KOH) or active charcoal. Iodine in the leachate or trapping solution is extracted with CCl_4 (or CHCl_3) after acidified and oxidized to I_2 , and then back extracted with H_2SO_3 . After conversion of separated iodine to MgI_2 , it is applied for neutron irradiation. Fig. 5 shows a commercial combustion facility, which can be used for separation of iodine from solid sample. For water sample including milk and urine, iodine can be separated by anion exchange method. In

**Fig. 4.** Diagram of analytical procedure for the determination of ^{129}I by radiochemical NAA.

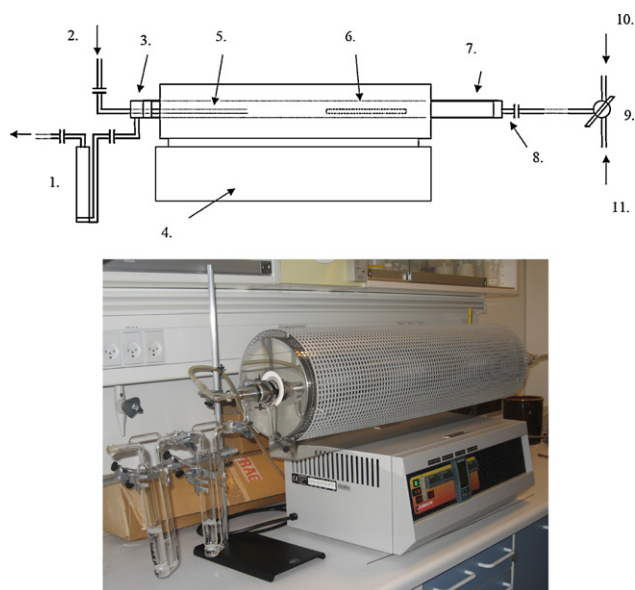


Fig. 5. Schematic diagram and picture of combustion facility (Carbolite, UK) for the separation of iodine from solid sample. (1) Gas bubbler (filling with NaOH solution for trapping iodine); (2) oxygen supply; (3) exhaust gas manifold; (4) temperature controller of combustion furnace; (5) second furnace (for complete combustion of residue from first furnace); (6) sample boat in the first furnace; (7) quartz working tube; (8) gas inlet adaptor; (9) three ways valve; (10) main oxygen supply; (11) compressed air supply (in the beginning of combustion, air is supplied to avoid a violet combustion under pure oxygen condition).

which, iodine is first converted to iodide and then absorbed by anion exchange resin (AG1) and separated from matrix elements. The iodide absorbed on resin is eluted by nitrate solution, and concentrated by extraction with CCl_4 from the eluate [16,23,36,123]. The separated iodine in small volume of water sample is converted to MgI_2 similar to solid samples.

The pre-separated iodine as MgI_2 or adsorbed in active charcoal is irradiated in a nuclear reactor for 2–12 h and the irradiated samples is further purified by dissolution with acid and then extracted with CCl_4 . Iodide is then precipitated as PdI_2 for gamma counting. The ^{130}I (from ^{129}I) and ^{126}I (from ^{127}I) are counted using an HpGe detector. By comparison with standard and correction for chemical yield during the chemical separation, the absolute contents of ^{129}I and ^{127}I in the samples are calculated.

^{127}I can also cause interference during the determination of ^{129}I by three continuous neutron capture reactions, $^{127}\text{I}(3n, \gamma)^{130}\text{I}$. This interference varies as the square root of the neutron flux and increases with the length of the irradiation time. For irradiation of 10 h in a thermal neutron flux of $4 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$, 1 g of ^{127}I can produce ^{130}I equivalent to $7.7 \times 10^{-12} \text{ g}$ of ^{129}I . For a sample with $^{129}\text{I}/^{127}\text{I}$ ratio higher than 10^{-11} , this interference can be corrected by simultaneous determination of ^{127}I concentration via a fast neutron reaction of $^{127}\text{I}(n, 2n)^{126}\text{I}$. But, this interference limits the analysis of sample with $^{129}\text{I}/^{127}\text{I}$ ratio lower than 10^{-11} .

A large number of samples have been analyzed for ^{129}I using NAA [13,14,16,22,23,35,36,77,85,86,113–116,118–121], and NAA is also a main method used for the determination of ^{129}I in environmental samples besides AMS. A detection limit of $1 \mu\text{Bq}$ (or $2 \times 10^{-13} \text{ g}$, or 10^9 atoms, or $^{129}\text{I}/^{127}\text{I}$ ratio of 10^{-10}) has been reported [120].

4.4. Accelerator mass spectrometry (AMS)

Mass spectrometric techniques, including AMS, SIMS and ICP-MS, have also been used for ^{129}I determination. Almost all AMS

facilities can be understood as two mass spectrometers (called “injector” and “analyzer”) linked with a tandem accelerator. Before measurement, iodine needs to be separated from the sample and prepared as AgI precipitate. The separation procedure used in the NAA can be also used for AMS. The separated iodine as iodide is then precipitated as AgI , which is dried and then mixed with Ag or Nb powder for AMS measurement. The iodine in AgI target is injected to the system as a negative ion by ion sputtering (e.g. using a Cs^+ primary ion source), I^- ions are easily formed in the sputter source, while $^{129}\text{Xe}^-$, the main isobaric interference, is unstable and decomposed rapidly thus having insignificant interference. The formed $^{129}\text{I}^-$ and $^{127}\text{I}^-$ negative ions are then accelerated to positive high-voltage terminal of a tandem accelerator where several electrons may be stripped off, converting negative ions to I^{3+} , I^{5+} or I^{7+} . The stripping process has the advantage that it dissociates molecular ions if enough electrons are stripped off which results in a further elimination of interferences from $^{128}\text{TeH}^-$ and $^{127}\text{IH}_2^-$. The positively charged ions from the accelerator then pass through a magnetic analyzer, where the ions of ^{129}I and ^{127}I with a well defined combination of charge state and energy are selected, and directed to a detector. Furthermore, the higher energies of the ions after acceleration allow an additional separation of the wanted ions from possible background ions at the particle detector. The separated ^{129}I is detected by a combination of time-of-flight and silicon charged particle detectors or gas ionization energy detector. The instrumental background of $^{129}\text{I}/^{127}\text{I}$ down to 10^{-14} has been obtained [124]. The detection limit of ^{129}I depends on the chemical separation procedure and iodine carrier. Commonly a blank $^{129}\text{I}/^{127}\text{I}$ ratio of 1×10^{-13} was reported, which corresponds to 10^{-9} Bq (or 10^{-16} g or 10^5 atoms) ^{129}I for 1 mg ^{127}I carrier, and the analytical uncertainty is lower than 10% for a $^{129}\text{I}/^{127}\text{I}$ ratio of 10^{-12} [124]. Due to the very high sensitivity, most of determinations of ^{129}I in environmental samples, especially low level geological samples, are now carried out by AMS. Actually, AMS is the only method for the determination of ^{129}I in the pre-nuclear age samples ($^{129}\text{I}/^{127}\text{I} < 10^{-10}$) [4,6–12,15,17,18,26,52,39,45,56,82–84,89,90,94,103,108,126–128]. AMS is a relative analytical method, $^{129}\text{I}/^{127}\text{I}$ ratio is normally measured, and the ^{129}I absolute concentration is calculated by the ^{127}I content in the samples. For the samples with a $^{129}\text{I}/^{127}\text{I}$ ratio higher than 10^{-10} , a large amount of ^{127}I carrier (1–2 mg) comparing to the ^{127}I content in the sample itself ($< 10 \mu\text{g}$) is normally added to the sample before chemical separation, the ^{129}I concentration is then calculated by the ^{127}I added and the measured $^{129}\text{I}/^{127}\text{I}$ ratio. While for the sample with a low $^{129}\text{I}/^{127}\text{I}$ ratio ($< 10^{-13}$ to 10^{-10} , pre-nuclear age sample or less contaminated by human nuclear activity such as deep seawater, soil or sediment from deep layer), a carrier free iodine needs to be separated because of interference of ^{129}I in the ^{127}I carrier (10^{-13} for $^{129}\text{I}/^{127}\text{I}$ ratio for low background iodine carrier, such as iodine supplied by Woodward Iodine Corp. USA). For the high iodine concentration samples, such as brine, seaweed and thyroid, the carrier free ^{129}I may be easily separated, but for low iodine concentration sample, such as fresh water, terrestrial plant and animal sample ($< 5 \text{ ng mL}^{-1}$ water or $1 \mu\text{g g}^{-1}$ plant or animal sample), it is difficult to separate enough amount of carrier free iodine ($150 \mu\text{g}$) [129]. Yiou et al. [130] reported a method for prepare carrier free iodine from seawater. In this method, silver powder is first added to the water, iodine species is then adjust to molecular iodine (I_2) and the water is stirred for 10–20 h, iodine is consequently absorbed on silver powder and separated from the seawater. The method is very simple to operate and very useful for the separation of inorganic iodine from the seawater without carrier added. However, the volume of the sample is small (100–250 mL), it is therefore not sufficiency for the analysis of low level ^{129}I sample, which

needs a large sample. In addition, the recovery of iodine is also lower (<50%).

4.5. Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS has also been used for the determination of ^{129}I [131–136]. In this method, iodine separated from the samples is introduced to the machine as solution or gaseous iodine (I_2). The separation method used in NAA (Section 4.3) can be also used for the separation of iodine from the samples.

In ICP-MS, iodine introduced to the plasma is decomposed into iodine atom and ionized to positive iodine ion at a temperature of approximately 6000–8000 K. Due to higher ionization potential (10.45 eV), ionization efficiency of iodine is normally lower comparing to metals, which results in a lower analytical sensitivity of iodine. The positively charged iodine is extracted from the plasma (at atmospheric pressure) into a high vacuum of the mass spectrometer via an interface. The extracted ions are then separated by mass filters of either quadrupole type time-of-flight or combination of magnetic and electrostatic sector, and finally measured by an ion detector.

Problems associated to the determination of ^{129}I using ICP-MS is low sensitivity (low ionization efficiency), isobaric and molecular ions interferences (^{129}Xe , $^{127}\text{IH}_2$, $^{89}\text{Y}^{40}\text{Ar}$, $^{115}\text{In}^{14}\text{N}$, $^{113}\text{Cd}^{16}\text{O}$), memory effects, low abundance sensitivity of ICP-MS (tailing from the ^{127}I peak), especially isobaric ^{129}Xe interference and tailing of ^{127}I . A dynamic reaction cell (DRC) ICP-MS by using oxygen as reaction gas has been found to significantly reduce signals of xenon ions by charge transfer. It was also found that pressurizing the collision cell with helium the tailing of ^{127}I or abundance sensitivity can be improved. By using helium and oxygen in the DRC, and directly introducing gaseous iodine to the ICP-MS system, the detection limit of ICP-MS could be significantly improved to 10^{-6} for $^{129}\text{I}/^{127}\text{I}$ ratio (or $25 \mu\text{Bq g}^{-1}$ for ^{129}I at a ^{127}I concentration of $4 \mu\text{g g}^{-1}$) [134]. By trapping gaseous iodine thermally released from samples, and then desorbing it into the ICP-MS system, detection limit could be further improved to $2.5 \mu\text{Bq g}^{-1}$ (or 10^{-7} for $^{129}\text{I}/^{127}\text{I}$ ratio) [135]. By using a similar technique, but directly introducing water samples in 1% tertiary amine carrier solution, a detection limit of $37 \mu\text{Bq mL}^{-1}$ was reported [136].

Table 3 compares various analytical methods for the determination of ^{129}I . The X- γ -spectrometry and LSC are the least sensitive and long counting time, while they are cheaper and good accessible. These methods are therefore only suitable for the analysis of nuclear waste and high level environmental samples ($^{129}\text{I}/^{127}\text{I}$ higher than 10^{-6}). By using DRC techniques, ICP-MS can be used for the determination of ^{129}I , but the detection limit for $^{129}\text{I}/^{127}\text{I}$ is only 10^{-7} , it may only be suitable for the analysis of high level environmental samples. Only NAA and AMS are sensitive enough for the analysis of environmental samples ($^{129}\text{I}/^{127}\text{I}$ ratio of $10^{-6} \sim 10^{-10}$),

in which AMS is the only method for analysis of per-nuclear age samples with $^{129}\text{I}/^{127}\text{I}$ ratio lower than 10^{-10} .

5. Speciation analysis of ^{129}I in environmental and biological samples and its application

In principle, method for speciation of ^{129}I in the environment should be the same as for stable iodine considering the natural sources and assuming isotopic equilibrium. However, as described above, the naturally occurred ^{129}I (generated from the uranium fission and cosmic ray reaction of Xe) is overwhelmed by the anthropogenic ^{129}I from the human nuclear activity since 1945, especially the release from the reprocessing plants since 1990s. This situation has created isotopic disequilibrium between ^{127}I and ^{129}I in the environment, which may partly result from a different distribution of ^{129}I species compared to stable iodine (^{127}I). Although there are a number of reports on the speciation analysis of stable iodine, data on ^{129}I speciation is still scarce. The extremely low concentration of ^{129}I in the environment compared to stable ^{127}I ($^{129}\text{I}/^{127}\text{I}$ lower than 10^{-6}) requires a large sample for the analysis of ^{129}I species, which makes application of the conventional method used for speciation analysis of stable iodine impractical for ^{129}I . New separation procedures have to be developed for ^{129}I speciation analysis, which is reviewed below with comments on their potential applications.

5.1. Speciation of ^{129}I in water

In seawater, iodine exists mainly as iodide and iodate with a minor organic iodine and consequently speciation analysis of iodine in seawater commonly focus on iodide and iodate. Hou et al. [23] has developed a chemical procedure for the separation of iodide and iodate from large seawater samples (up to 50 L). The method is based on different affinities of iodide, iodate and other anions, such as Cl^- and Br^- , on anion exchange column. Iodide with a strong affinity is absorbed on the column, while iodate with a low affinity pass through the column or very weakly adsorbed on the column with Br^- and Cl^- . These anions can easily be removed from the column by using low concentration of nitrate ($<0.5 \text{ mol L}^{-1}$). The adsorbed iodide on the column is eluted using high concentration of nitrate ($1.5\text{--}2.0 \text{ mol L}^{-1}$). Converting the anion exchange resin to nitrate form instead of chloride form enhances the capacity of the anion exchange column for iodide by 5–10 times, which is a useful approach for analysis of large seawater sample. The iodate in the effluent and wash (with Br^- and Cl^-) is then converted to iodide by addition of NaHSO_3 and acidifying to pH 2–3 using HCl. The solution is then passed through another anion exchange column, where the iodide absorbed on the column is eluted using $2.0 \text{ mol L}^{-1} \text{ NaNO}_3$ for the determination of iodate. The iodide in nitrate eluate is then concentrated using CCl_4 or CHCl_3 extraction following the same procedure for extraction of total ^{129}I (Section 4.3). The separated

Table 3
Comparison of measurement methods for the determination of ^{129}I .

Detection method	Target preparation	Detection limit		Reference number
		Bq	$^{129}\text{I}/^{127}\text{I}$ ratio	
X- γ spectrometry	Direct measurement	100–200 mBq	10^{-4} to 10^{-5}	[106]
X- γ spectrometry	Separated iodine (AgI)	20 mBq	10^{-5} to 10^{-6}	[117]
LSC	Separated iodine	10 mBq	10^{-5} to 10^{-6}	[117]
RNAA	Separated MgI_2/I_2 absorbed on charcoal	1 μBq	10^{-10}	[120]
AMS	AgI	10^{-9} Bq	10^{-13}	[124]
ICP-MS	Direct water measurement	$40\text{--}100 \mu\text{Bq mL}^{-1}$	10^{-5} to 10^{-6}	[136]
ICP-MS	Gaseous iodine	$2.5 \mu\text{Bq g}^{-1}$	10^{-7}	[135]

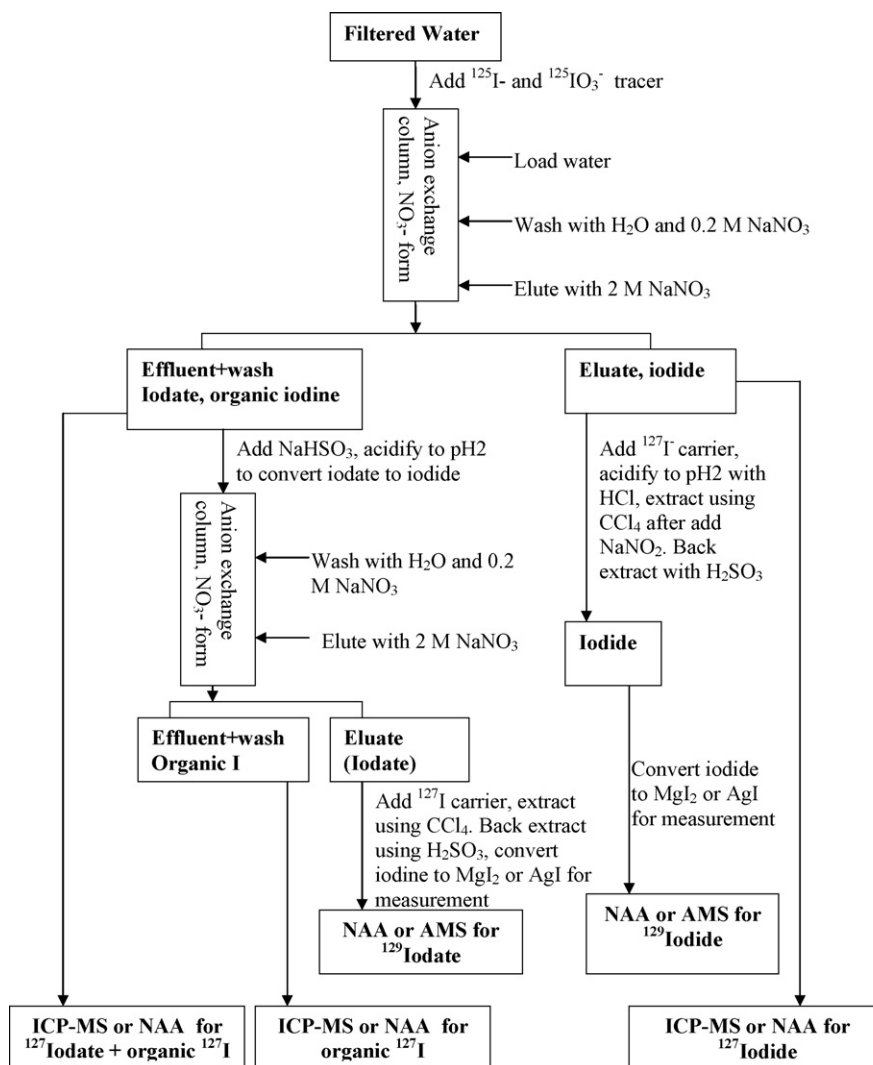


Fig. 6. Chemical procedure for speciation analysis of iodine in water sample.

^{129}I in iodide and iodate is then measured using NAA or AMS [13,23]. A schematic flow chart of the analytical procedure is shown in Fig. 6. However, organic ^{129}I cannot be determined in this procedure. Schwehr et al. [17] proposed a procedure for the determination of organic ^{129}I where water sample is first digested by heating under ultrasonic condition in NaOH and ethanol medium. This step is supposed to decompose all organic matters and iodine in organic form would be released and converted to inorganic iodine. Later an anion exchange chromatography and CCl_4 extraction are used to extract total ^{129}I . The organic ^{129}I in the sample is then calculated by the difference between total ^{129}I and the sum of $^{129}\text{I}^-$ and $^{129}\text{IO}_3^-$. For water from estuaries, rivers and lakes, the concentration of organic ^{129}I may be significant comparing to iodide and iodate for which the procedure described above can be also used. In addition, the total ^{129}I can also separated by evaporation of fresh water to dryness and decomposition of residue by digestion or combustion, following the extraction and precipitation as MgI_2 or AgI [166].

Anion exchange chromatography is a good method for the separation of iodide and iodate, and has been successfully applied for the analysis of seawater and fresh water in the laboratory. However, the procedure is time consuming and not practically suitable for treatment of water samples in the field and on board sam-

pling vessels. It is recommended that speciation analysis, especially the separation part, to be carried out during a short time after the sampling. In addition *in situ* separation can meet the requirement of analysis of large number of samples without a problem of transport (shipping, etc.) to get the samples back to the laboratory. Accordingly, a new and simple speciation method has been developed using AgCl co-precipitation for the speciation analysis of ^{129}I in seawater. In this method, $^{125}\text{I}^-$ tracer and $^{127}\text{I}^-$ carrier are first added to the seawater and the pH of sample is adjusted to 4–6 using HCl . AgNO_3 is added with a ratio of $\text{Ag}:\text{Cl}$ less than 100, and $\text{Ag}:\text{I}$ higher than 5. After stirring for 0.5–1 h, AgI precipitated with AgCl is then separated by decanting the supernatant after settling down and centrifuging. The AgI is afterwards separated from AgCl by addition of NH_3 to dissolve AgCl , and centrifuge. The separated AgI is used for AMS measurement of $^{129}\text{I}^-$ after dryness [134]. For the determination of total inorganic ^{129}I , the sample is acidified to pH 2 after addition of NaHSO_3 and the iodate, which was converted to iodide, is then separated with iodide using the same method as for $^{129}\text{I}^-$. The concentration of $^{129}\text{IO}_3^-$ is calculated by the difference between total inorganic ^{129}I and $^{129}\text{I}^-$. The ^{125}I tracer experiment showed that the recovery of iodine in this method is higher than 85%, and cross contamination of $^{129}\text{I}^-$ and $^{129}\text{IO}_3^-$ is less than 2% [137]. This separation

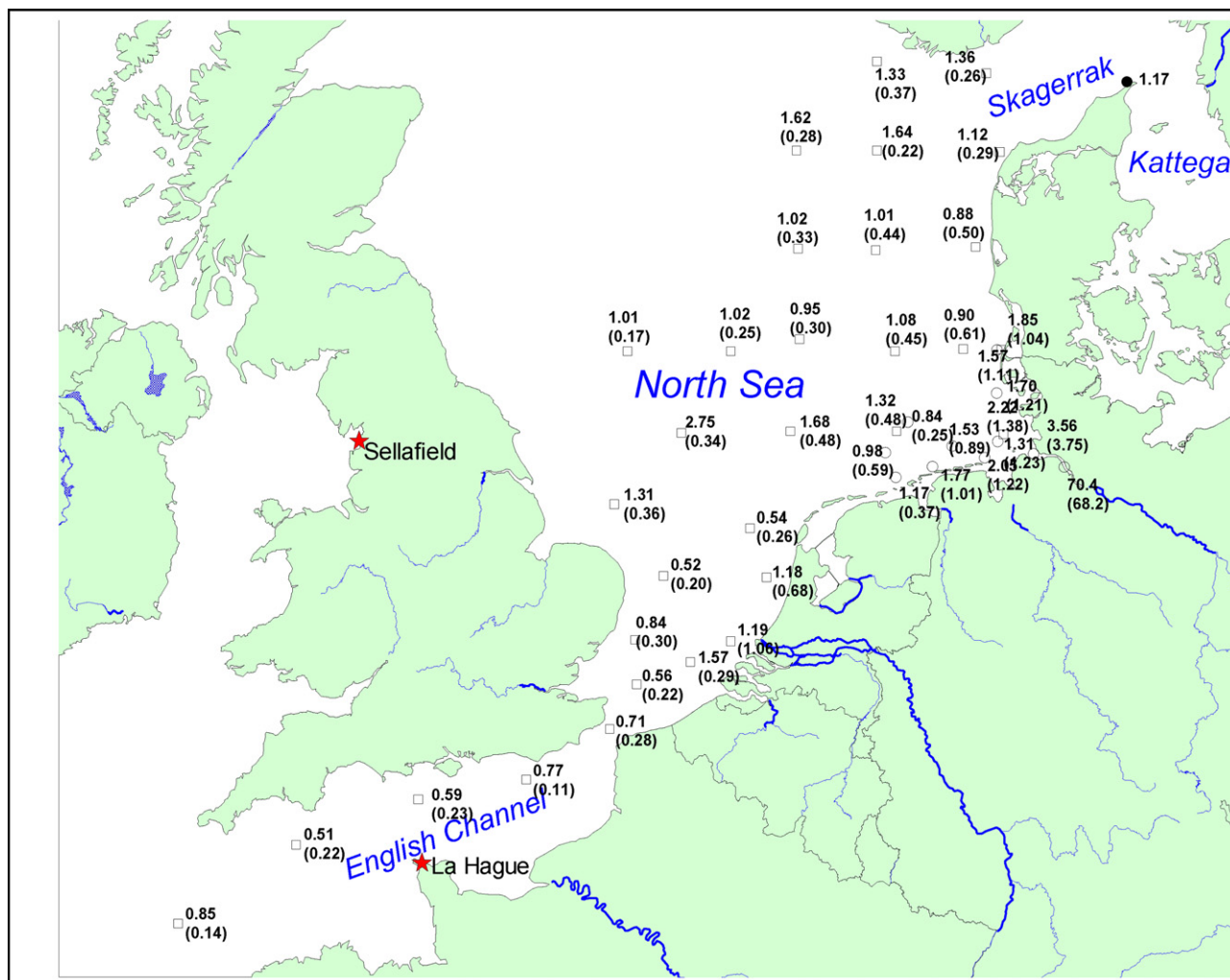


Fig. 7. Distribution of iodide/iodate ratios for ^{129}I (upper number) and ^{127}I (in parentheses) in Seawater from the English Channel and North Sea.

method is suitable for the *in situ* work in the field or on board of a ship.

^{129}I discharged from reprocessing plants at La Hague and Sellafield has been used as a specific source of ^{129}I in the Nordic seawater. The signal of ^{129}I is used as a tracer to investigate marine geochemical cycle of stable iodine and in particular for conversion mechanisms of different chemical species of iodine as well as distinguishing newly produced from converted iodine species. Hou et al. [15,23] have measured iodide and iodate in seawater collected from the English Channel, North Sea, as well as Kattegat and Baltic Sea. The ratios of iodide/iodate for ^{129}I and ^{127}I in these waters are shown in Fig. 7, which indicates significantly different speciation distribution for ^{129}I and stable iodine (^{127}I). It was concluded that: (1) a rapid reduction of iodate to iodide occurs along the European continental coastal area, (2) oxidation of the new produced iodide to iodate does not occur during its transit along the European continental coast and (3) reduction of iodate or oxidation of iodide in the open sea seems to be a slow process [15]. The ratio of $^{129}\text{I}/^{127}\text{I}$ for iodate in the Baltic seawater is much higher than that for iodide and close to the level in the Kattegat. This result suggests that ^{129}I in the iodate form in Baltic Sea water seems originated from the Kattegat, and implies a slow reduction process of iodate in the Baltic Sea.

River flood can also provide ^{129}I in the estuary areas as observed by speciation analysis of ^{129}I and ^{127}I in Galveston Bay, Texas, USA [17]. Organic ^{129}I from the terrestrial source was observed in water with salinity up to about 20 within the Bay area, which agrees with the observation from stable isotopes, such as ^{13}C and ^{14}N , and suggested that organic ^{129}I can be used as a tracer for the dissolved organic carbon in coastal zones.

5.2. Speciation of ^{129}I in atmosphere

As mentioned above, iodine in the atmosphere exists as particle associated, inorganic gaseous iodine (such as I_2 , HI , HIO) and organic gaseous iodine (CH_3I , CH_2I_2 , $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$, etc.). Due to very low concentration of ^{129}I in the atmosphere, the determination of individual species of ^{129}I is difficult. The speciation analysis of ^{129}I is mainly focused on the determination of three fractions of ^{129}I (particle associated, inorganic and organic gaseous ^{129}I) [20,138], as well as the distribution of ^{129}I in different size of particulates [139]. The main technique used for collection of three fractions of ^{129}I is illustrated in Fig. 8 (Hou, unpublished). The sampler consists of multistage collector/trapper which is finally connected to a vacuum pump. Particle associated iodine is first collected by a membrane with small size pore ($<0.45\ \mu\text{m}$), the

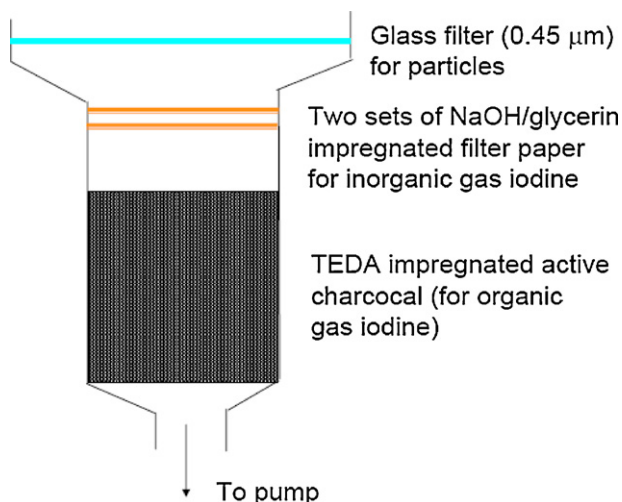


Fig. 8. Diagram of air sampler for collecting particle associated iodine, inorganic gaseous iodine and organic gaseous iodine.

gaseous iodine pass through the membrane, of which inorganic species, such as I_2 and HI , is then trapped by cellulose filter papers previously impregnated with $NaOH$ /glycerin. For completely trapping of the inorganic gaseous iodine, two cascade filter papers are used. Following the filter papers, an active charcoal column with length of 2.5 cm is used for trapping organic gaseous iodine. To obtain a sufficient trapping efficiency, the active charcoal was previously impregnated with tetrabutylammoniumhydroxide (TBAH) or triethylenediamine (TEDA) solution. Experiments have shown a satisfactory separation of three fractions of iodine [70,71]. Iodine in the collected fractions is then separated by combustion using a tube oven (Fig. 5), and trapped in $NaOH$ solution, then extracted using CCl_4 or $CHCl_3$ and prepared as MgI_2 or AgI for measurement. Besides ^{129}I , stable iodine in the atmosphere is normally also required in order to obtain the $^{129}I/^{127}I$ value, which is more useful instead of only ^{129}I concentration. In this case, the stable iodine blank in collecting materials, such as filters, active charcoal, TBAH and/or TEDA is very important. A low iodine blank charcoal and chemical reagent have to be chosen. A low iodine content TEDA (Sigma, Germany) with iodine concentration of 6.5 ng g^{-1} was used in the author's laboratory, comparing with a similar reagent of TBAH (20% solution in water for synthesis, Merck, Germany) with an iodine concentration of 164 ng mL^{-1} . In addition, for reducing iodine blank in active charcoal, $NaOH$ solution leaching and heating at high temperature ($900\text{--}1000^\circ\text{C}$) under nitrogen condition have been used [71], however, our experiment showed that only less than half of iodine in the charcoal can be removed by these methods. It is therefore better to find a low iodine blank charcoal. A low iodine content active charcoal (for chromatography, Merck, Germany) was used in the author's laboratory, in this charcoal, the total iodine concentration of only 40 ng g^{-1} was measured, after washing with $NaOH$ solution, the iodine concentration was reduced to 30 ng g^{-1} . The concentration of iodine in TEDA impregnated charcoal was measured to be only 45 ng g^{-1} , which is more than 30 times lower than the commercial TEDA impregnated charcoal specific designed for trapping radioactive iodine (TEDA Carbon Cartridge, The Staplex Company, Brooklyn, USA), we have measured iodine concentration in this charcoal to be 1400 ng g^{-1} .

Several investigations have been carried out to measure different species of ^{129}I in atmosphere. Wershofen and Aumann [20] have measured ^{129}I and ^{127}I in three fractions in the atmosphere

collected from locations with varying distance (0–23 km) to the WAK reprocessing plant in Germany. They observed a different distribution of ^{129}I and ^{127}I in these three fractions. Particle associated ^{129}I ranges at 2–30% of total ^{129}I , while the corresponding ^{127}I ranges at 12–28% of total iodine. The gaseous inorganic ^{129}I fraction ranges at 17–35% while the ^{127}I is 1.5–27%. Similarly large variation is found between gaseous organic ^{129}I (34–98% of total ^{129}I), and ^{127}I (46–74% of total iodine). It was also noticed that the closer the location to the reprocessing plant, the higher the percentage of gaseous organic ^{129}I , while no such a trend was observed for ^{127}I . This feature indicates that equilibrium between ^{129}I and ^{127}I in the atmosphere takes long time due to different sources and species. ^{129}I species in the atmosphere near the Sellafield reprocessing plant (1.3 km northern northwest) was also measured. It was found that 63–100% of ^{129}I was organic gaseous ^{129}I , while inorganic gaseous and particle associated ^{129}I compose less than 21% and 17% respectively (Ferozan, personal communication). Although direct measurement of ^{129}I species in the atmosphere from the stack in reprocessing plants is not available, it was estimated that in one stack in Sellafield reprocessing plant, 70% iodine was released as inorganic ^{129}I (mostly I_2) and 30% of organic ^{129}I . In another stack in the same reprocessing plant, 100% ^{129}I is released as organic ^{129}I (Ferozan, personal communication). However, the measured ^{129}I in the environment was mainly organic gaseous ^{129}I [20, Ferozan, personal communication].

Comparing with ^{129}I released to the atmosphere from the stacks in reprocessing plants, a large amount of ^{129}I has been discharged to the English Channel from La Hague reprocessing plant and to the Irish Sea from Sellafield reprocessing plant (Fig. 2). It is well known that iodine in the ocean is emitted to the atmosphere as methyl iodide and other gaseous forms, which may contribute to the ^{129}I load in the atmosphere. It has been accepted for a long time that iodine in the ocean is the main source of iodine on land [137,140]. However, recent data suggest that releases from the terrestrial pool, vegetation and soil can add significant amounts to the atmosphere [141,142]. It was also argued that comparable iodine deposition in the coastal and the inland areas suggests that iodine flux to soil from terrestrial plant release is comparable to those from the ocean [141,142]. One measurement of ^{129}I species in atmosphere over the North Sea has been carried out indicating that particle associated, inorganic and organic gaseous ^{129}I were 18%, 43% and 40% respectively, with a similar distribution for ^{127}I . The $^{129}I/^{127}I$ values in different fractions were significantly different with the highest value (8.4×10^{-7}) in particle, lowest value in inorganic gas fraction (1.2×10^{-7}) and 3.1×10^{-7} in organic gas fraction [39]. This indicates different sources of ^{129}I and ^{127}I in the atmosphere and also shows that ^{129}I can be used as a potential tracer for the geochemical cycle of stable iodine such as transfer of iodine from ocean to atmosphere, soil, plant and humans.

During the Chernobyl accident, a large amount of radioactivity was released to the atmosphere, including ^{129}I , ^{131}I , and other iodine radioisotopes. Unfortunately, data on ^{129}I speciation in the source plume from the accident is not available, but it was supposed that most of ^{129}I and ^{131}I have been released as I_2 . Measurements carried out in Lithuanian and Japan for speciation of ^{129}I and ^{131}I during the Chernobyl accident [70,138] indicated that 60–80% was observed in organic gaseous form, whereas the inorganic gas composes less than 10%, and the particle associated form is less than 35%. The high fraction of organic form of ^{129}I and ^{131}I may be attributed to conversion during long distance (longer time) transport of the radioactive plume.

The availability of radionuclides in the atmosphere is not only related to their species, but also to the size of the particles. The size distributions of ^{129}I and ^{131}I associated particles in the

atmosphere have been investigated using cascade impactor air sampler [139,143,144]. It was observed that ^{129}I and ^{131}I are mainly associated with fine particles, with a ^{129}I activity median aerodynamic diameter (AmAD) of $0.4\text{ }\mu\text{m}$ [139]. A similar distribution pattern was also observed for ^{131}I originated from the Chernobyl accident (with an AmAD of $0.2\text{--}0.4\text{ }\mu\text{m}$) [143,144].

5.3. ^{129}I speciation in soil and sediment

Direct measurement of iodine speciation in soil and sediment is normally difficult, but techniques such as X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure spectra (EXAFS) have been utilized. The relatively low concentration of ^{129}I in the environment and the low sensitivity of XANES and EXAFS make direct measurement of ^{129}I even more difficult. Therefore, sequential extraction or selective extraction is normally applied for separation of different components (speciation) of soil and sediment. A sequential extraction procedure that was proposed by Tessier et al. [145] has found wide applications. In this method the iodine was separated as water-soluble, exchangeable, carbonate, metal oxides (reducible), organic bound, and residue (mineral bound). Because iodine is easily volatile in acidic and oxidizing condition, modification of the original procedure has to be performed in order to avoid iodine loss during the extraction.

For the sequential extraction separation, the batch method is normally applied for easy operation and apparatus requirement. However, this method is time consuming, steady state leaching process and is associated with risk of cross contamination and re-adsorption. To overcome these shortages, a dynamically extraction method was therefore proposed for sequential extraction of some radionuclides [146], and has been applied for iodine fractionation/speciation in soil and sediment samples in the authors' lab.

In the batch sequential extraction procedure, the water-soluble iodine is first extracted using water and the leachate is separated by centrifuge. Remained solid is then treated with CaCl_2 , MgCl_2 or NH_4OAc solution (pH 7–8) to recover exchangeable fraction. Remained residue from this treatment is extracted again using NH_4OAc , but at pH 5 for carbonate. All these steps are operated at room temperature. Afterward, the oxyhydroxides (or reducible) fraction is extracted using $\text{NH}_2\text{OH}\cdot\text{HCl}\text{--}\text{HOAc}$ at pH 2 and the remained sample is finally extracted for organic fraction using $\text{H}_2\text{O}_2\text{--}\text{HNO}_3$ at pH 2 or NaOH or $\text{NH}_2\text{OH}\cdot\text{HCl}\text{--}\text{carbonate}$ (pH 8–9). These two steps are carried out at $80\text{--}100\text{ }^\circ\text{C}$. The remained fraction is treated as a residue. A schematic diagram of the whole procedure is shown in Fig. 9. Use of $\text{H}_2\text{O}_2\text{--}\text{HNO}_3$ for the extraction of organic fraction means that the iodine will be oxidized to I_2 and lost during the extraction. Therefore a use of NaOH (0.3 mol L^{-1}) or $\text{NH}_2\text{OH}\cdot\text{HCl}\text{--}\text{carbonate}$ is a recommended alternative method for extraction of iodine in organic fraction [21,77]. To completely destroying organic substances, treatment with NaClO decomposition is followed after the NaOH or $\text{NH}_2\text{OH}\cdot\text{HCl}\text{--}\text{carbonate}$ extraction [147]. Another approach is to extract the organic fraction using $\text{H}_2\text{O}_2\text{--}\text{HNO}_3$, but both residues (before and after the extraction) are analyzed for iodine and the difference in iodine content of these two samples is calculated as the organic fraction [36].

For soil or sediment with high organic matter content, the order of sequential extraction may be partly modified due to the wrapping of grains by organic matters that may reduce the extraction efficiency during the different steps, especially for the oxides fraction step. Additionally, the released iodine from the sample may be easily re-adsorbed to organic matters during oxidizing and acid condition. For this purpose, iodine associated to organic fraction may be extracted before the oxides fraction and after the carbon-

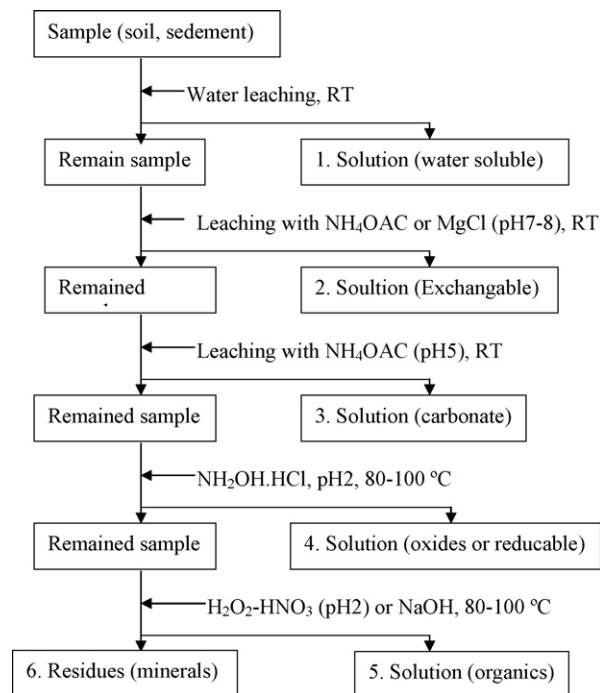


Fig. 9. Sequential extraction procedure for fractionation of iodine in soil and sediment samples.

ate fraction using NaOH or NaOCl . In this case, oxides component can be decomposed and iodine binding to this component can be completely released.

^{129}I in the separated fractions is then further purified by CCl_4 (or CHCl_3) extraction after conversion of all iodine to iodide form. For the organic fraction, if $\text{NH}_2\text{OH}\cdot\text{HCl}\text{--}\text{carbonate}$ or NaOH method is used, a further decomposition using NaOCl may be needed before the CCl_4 extraction. ^{129}I in the final residue can be separated using the same method as that for total ^{129}I in soil and sediment sample, i.e. combustion or alkali fusion, described in the Section 4.3.

Schmitz and Aumann [21] have analyzed soils collected from a region closed to the WAK reprocessing plant in Germany and found a relatively higher percentage of ^{129}I in water-soluble (39–49%), exchangeable (7–20%), and residue (25–70%) fractions compared to the organic (4–15%), oxides (7–13%) and carbonate (3–8%) fractions. However, a different distribution of stable iodine (^{127}I) was observed where only <4% occurs in the water-soluble fraction. This difference between ^{129}I and stable iodine may be attributed to the different sources of the two isotopes. ^{129}I has mainly short period anthropogenic sources, while ^{127}I has both natural and anthropogenic sources and resided in the soil for a relatively long time. This implies that chemical equilibrium between ^{129}I and stable ^{127}I within the soil environment may take a long time and resulting in different speciation patterns with respect to mobility and bioavailability of the two isotopes. Apparently, this result shows that ^{129}I in the soil is more mobile and bioavailable than ^{127}I .

Another distribution pattern of ^{129}I is observed in the soil and sediment collected from coastal and estuarine area around the Sellafeld reprocessing plant [76] compared to that observed in the soil from near the WAK reprocessing plant [21]. Higher percentage of ^{129}I was found in oxides (53–66%) and organic (23–43%) fractions, whereas only <7.5% was found in the other fractions (the residue was not included). A similar result was also obtained from soil sample (2–4 cm depth) collected from the Chernobyl accident contaminated area (10 km to Chernobyl power plant) and in sediment from the Irish Sea. In both materials, ^{129}I in the oxides (30–40%) and

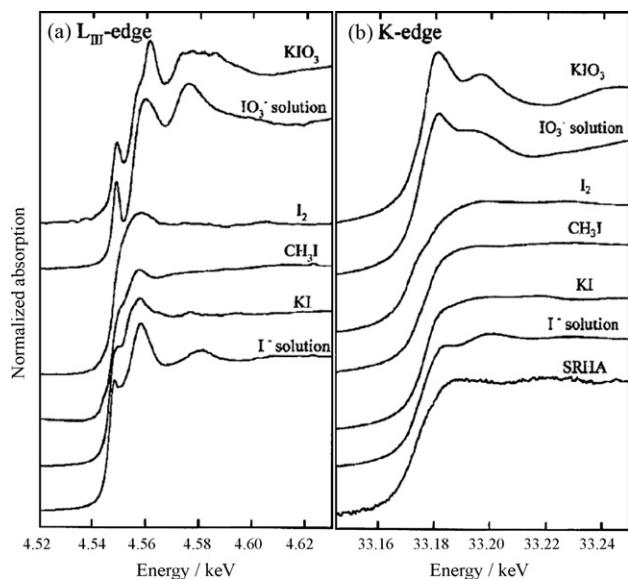


Fig. 10. Iodine L3-edge (a) and K-edge (b) XANES spectra of different iodine species reference materials [152].

organic (40–48%) fractions is higher than in the water-soluble fraction (6–13%) [22]. Results from sediment samples (organic content >50%) collected from a lake (in central Sweden) showed that most ^{129}I is bound to the organic fraction (50–85%), whereas the water-soluble, exchangeable and carbonate fraction contain 5–8%, but relatively higher than ^{127}I (2–4%). The oxides-related fraction contains <2% of ^{129}I and ^{127}I respective total content [147]. The different distribution of ^{129}I in the near source area materials (Chernobyl, Sellafield and WAK) compared with far from source materials (central Sweden) may relate to conversion of ^{129}I species upon transport as well as environmental conditions at the sampling site.

Besides fractionation, the chemical speciation of iodine in leachate, especially in water-soluble and exchangeable fraction can be carried out to investigate the chemical forms of iodine in soil and sediment sample. The method used for the speciation of iodine in water sample can be used for this purpose. Yuita [78] has investigated the chemical speciation of stable iodine in soil solution (water-soluble), high iodide percentage was observed in flood and anoxic condition, while iodate is the dominant species in non-flood and oxidizing condition. Data on the ^{129}I speciation in soil solution are still lacking.

The direct measurement of *in situ* iodine speciation, especially in solid sample, is performed using XANES and EXAFS, which can be used to provide information on the local structure, coordination number and oxidation state of a range of elements in solution, solid form or at a solution–solid interface [147–149]. Using XANES a high intensity monochromatic X-ray beam (usually provided by a synchrotron source) is tuned through a range of energies from a few tens of eV below to about 100 eV above the binding energy of a core electron (e.g. iodine K-edge 33.17 keV and iodine L3-edge 4.557 keV) while keeping the beam on the same spot on the sample. The attenuation of the X-rays varies smoothly with incident energy until a critical energy is reached (i.e. core electron binding energy) and absorption (and fluorescence) abruptly increases. This discontinuity corresponds to the ejection of a core electron from an atom and is called the absorption edge, while the main absorption feature is referred to as the white line. The energy position of the white line is characteristic of the excited atom. The fine structure and position of the absorption edge can reveal information on the oxidation state of the element and its chemical surrounding (Fig. 10). This can readily

be utilized as a “fingerprinting” technique by comparing reference samples with unknown samples [100]. Further speciation information can be obtained at the same time by extending the energy range (~50–1000 eV above absorption edge) over which the data are collected, i.e. EXAFS (the entire structured absorption region (XANES + EXAFS) is also referred to as XAFS). EXAFS can give additional information on the coordination numbers and bond lengths to first, second and even more distant neighbor atoms [150]. However, EXAFS works best for ideal systems and information on the local structure is often needed before beginning an analysis [151].

Shimamoto and Takahashi [152] found that despite iodine K-edge XANES profiles are relatively featureless compared to those of L_{III} XANES, analysis of soil with iodine concentrations of $55 \mu\text{g g}^{-1}$ and high Ca concentrations in particular, should preferably be carried out at the K-edge because of the lower detection limit (avoiding the interference of Ca K X-rays with $\text{I L}\alpha$). They identified that the iodine in the soil is mainly as organic form. However, the detection limit of XANES is too high ($>10 \mu\text{g g}^{-1}$ or $>70 \text{Bq g}^{-1}$ for ^{129}I) to measure ^{129}I in environmental samples. Reed et al. [100] utilized iodine K-edge XANES in an attempt to identify the speciation of 10–100 ppm concentrations of ^{129}I ($70\text{--}700 \text{Bq g}^{-1}$) in nuclear waste reprocessing solvent (tri-*n*-butyl phosphate in odourless kerosene (TBP/OK)) from Sellafield reprocessing plant. The XANES profile of the waste sample resembled those of organoiodide reference samples. However, the presence of some molecular iodine could not be excluded due to the similarities between organoiodide and I_2 XANES spectra and poor statistics related to low concentrations. Other inorganic species of iodine appears to be relatively easy to deduce from organic species because they tend to have more structure in the post-edge region [100]. Employing I L_{III} XANES and EXAFS, Schlegel et al. [153] were able to show that iodine in naturally iodinated humic substances is aromatic-bound. XANES and EXAFS are qualitative analytical techniques, which means that information on distribution of different species of elements or radionuclides could not be supplied. Artifacts in XANES experiments due to radiation damage have been reported for several types of samples [154] and elements including iodine [152]. To monitor possible beam damage, energy scans repeated several times for each position of interest may be compared.

5.4. ^{129}I speciation in biological samples

A large number of investigations have been carried out on the speciation of stable iodine, and on the determination of total ^{129}I in biological samples including seaweed, grass, and thyroid. However, to our knowledge, published data on the speciation of ^{129}I in biological samples are not available. The separation of different species of stable iodine in biological samples, such as blood, milk, urine, homogenate of tissues and extractions of plants is normally carried out by high performance liquid chromatography (HPLC), electrophoresis, and gel chromatography [57–60,62,155–157]. These methods are suitable for the species separation of stable iodine in biological samples, especially for organic species of iodine. However, the size of sample applied for the analysis is normally small (< 1 mL), which is not suitable for ^{129}I due to minute concentration compared to stable iodine in biological samples ($^{129}\text{I}/^{127}\text{I} < 10^{-6}$).

The speciation analysis of ^{129}I normally needs a large amount samples (>5 g) and the separation methods developed by Hou et al. [42,43,57] for seaweed and tissues are suitable for the speciation of ^{129}I . For tissue samples, various sub-cellular fractions of tissue are separated using gradient centrifugation, these fractions include nuclei, cytosol, mitochondria, lysosome, and microsome. The iodine-bound proteins in cytosol of tissue are separated using gel chromatography (exclusion chromatography) for different molecular size. For the speciation analysis of ^{129}I in

seaweed, various fractions such as water-soluble iodine, soluble organic iodine, iodide, iodate, and protein-, pigment-, polyphenol- or polysaccharide-bound iodine can be separated using the method developed by Hou et al. [42,43]. The soluble iodine was first separated from the seaweed by water leaching, iodide, iodate, and organic iodine in the leachate can be then separated by using the anion exchange method as that used for water samples (Fig. 4) [23]. To investigate combination of ^{129}I in different components, such as protein, polyphenol, and pigment, several procedures can be used [43]. The separated organic binding ^{129}I fractions needs to be decomposed to be converted into inorganic iodine, in which the ashing or combustion method described above can be used. The inorganic iodine is finally concentrated and purified by CCl_4 extraction and precipitated as AgI for AMS measurement.

6. Bioavailability and radiation toxicity of ^{129}I

The bioavailability of an element in the environment depends on its species. For ^{129}I , there are practically scattered or almost lack of data about this issue. The various values of transfer factor (concentration of element in plant divided by that in the soil it grows on) of ^{129}I from soil to the grass (from 0.07 to 2.9 dry/dry weight) may reflect the different species of ^{129}I in the soil [158]. It is expected that the water-soluble and exchangeable ^{129}I can easily be taken up by plants through root, while bound in other fractions, such as organic, oxides and minerals is more difficult to be taken up. However, uptake of iodine by leaves from atmosphere is also a main pathway of iodine in plants.

It was reported that the bioavailability of iodine through potassium iodide to human (or mammals) is 96.4%, while the bioavailability of iodine through organic forms such as moniodotyrosine is 80.0%. A high bioavailability of iodine in seaweed *Gracilaria verrucosa* and *Laminaria hyperborean* (80–99%) was also observed [159]. Jahreis et al. [160] investigated the uptake of iodine through diet in 12 women, and found that 89% of iodine was excreted in the urine, and 11% in the faeces. However, Wahl et al. [161] reported low uptake of iodine from normal diet where only 16–18% of the alimentary iodine was excreted in the urine. This may indicate that the type of diet and species of iodine in the foodstuff are factors affecting bioavailability of iodine to human. A relatively low water (or acid) leaching rate of iodine (28–40%) from vegetable (spinach and green seaweed) was reported by Hou et al. [43].

Iodine in food is digested and absorbed in stomach and small intestine and passes into blood. Inhaled iodine from the air is also transferred into blood. Most of iodine absorbed into the blood is concentrated in the thyroid, and small part of iodine is directly excreted to the urine depending on the total amount of iodine in the diet. Most of iodine (>80%) in the human body (or mammal) concentrated in the thyroid, which is therefore the target organ (to it a specific element or compound is concentrated) of iodine (including radioactive ^{129}I). An average iodine content in adult thyroid is 10–15 mg, essentially combined with thyroglobulin, which is breakdown to the hormones triiodothyronine (T_3) and thyroxine (T_4) and released to the blood and transferred to other body tissues. The thyroid takes up stable and radioactive iodine indiscriminately. Due to low beta and gamma energy of ^{129}I (Table 1), radiation toxicity of ^{129}I is therefore mainly related to internal exposure of the thyroid to the beta radiation of ^{129}I . However, long half-life of ^{129}I (1.57×10^7 years) means long-term and low dose exposure. ^{129}I concentration (or $^{129}\text{I}/^{127}\text{I}$ value) in thyroid can be supposed to be equilibrium with ^{127}I the diet. It was reported that the equilibrium dose rate of ^{129}I in the thyroid is $0.151 \text{ mSv Bq}^{-1} \text{ y}^{-1}$ and $0.0161 \text{ mSv Bq}^{-1} \text{ y}^{-1}$ for a 1-year-old child and an adult, respectively [162]. A value of 10^{-6} for $^{129}\text{I}/^{127}\text{I}$ ratio in thyroid means an amount of ^{129}I at about 10^{-9} g (or 6.55 mBq) and 10^{-8} g (or

65.5 mBq) on the assumption of 1 and 10 mg stable iodine in thyroid for the 1-year-old child and adult respectively. The corresponding equilibrium annual dose equivalent to the thyroid can be therefore calculated to be about $10^{-3} \text{ mSv y}^{-1}$ for both 1-year child and adult. In an environment without direct contamination from nuclear facilities, $^{129}\text{I}/^{127}\text{I}$ ratio is much lower than 10^{-6} , which implies an effective radiation dose to thyroid from the internal exposure of ^{129}I is less than $10^{-3} \text{ mSv y}^{-1}$. This value is 40 times lower than the U.S. NRC regulation dose limit of 0.04 mSv y^{-1} for combined beta and photon emitting radionuclide to the whole body or any organ, and even 1000 times lower than the annual radiation dose of about 1 mSv from natural background radiation [163]. The highest $^{129}\text{I}/^{127}\text{I}$ value reported is 10^{-4} , in areas close to nuclear facility such as reprocessing plants [77,98,104,105,108,113], which corresponds to an annual radiation dose of 0.1 mSv y^{-1} to the thyroid. This value is only about 2.5 times higher than the regulation dose limit of 0.04 mSv y^{-1} . All these calculations don't consider the uptake of stable iodine from the diet with low ^{129}I level. In order to prevent iodine deficiency disorder, iodine was supplied as iodinated salt or in other form to humans (and animals). $^{129}\text{I}/^{127}\text{I}$ value in the iodinated food is much lower than the environmental level because stable iodine used for this purpose is normally produced from low ^{129}I source ($^{129}\text{I}/^{127}\text{I} < 10^{-9}$). In this case the $^{129}\text{I}/^{127}\text{I}$ value in thyroid of humans or mammals will be significantly lower than the environmental level. This means a low radiation dose to the thyroid. Additionally, 10 times lower $^{129}\text{I}/^{127}\text{I}$ value has been reported in the human (and animal) thyroid compared to the surrounding environment [36]. This feature implies that even in regions with high $^{129}\text{I}/^{127}\text{I}$ value in the environment, the effective radiation dose of ^{129}I to human thyroid is still lower than the regulation dose limit at present level. It has been mentioned above that there is about 68,000 kg of ^{129}I stored in unprocessed spent fuel until 2005 which is 10 times more than the ^{129}I released to the environment (<6000 kg). With the increasing number of nuclear power reactors, more ^{129}I will be produced. If most of the spent fuel is going to be reprocessed, and ^{129}I is released to the environment, it may increase the ratio of $^{129}\text{I}/^{127}\text{I}$ to 10^{-3} . In such a case, the annual dose to the thyroid may reach to 1 mSv y^{-1} , which excess the regulation radiation dose limit of ^{129}I to thyroid (0.04 mSv y^{-1}) and comparable to the level of natural background radiation. Accordingly, from the view of radiation dose, ^{129}I is less toxic at the present level or even higher level in the future. Le Guent et al. [164] estimated the radiation dose in a situation of high ^{129}I exposure through diet and drinking water and found that the estimated effective dose is only 30 and 60 mSv y^{-1} at an uptake of $153 \mu\text{g } ^{129}\text{I}$ per day for a 1-year child and an adult, respectively.

7. Summary and perspectives

The human nuclear activities, especially the releases from the spent nuclear fuel reprocessing plants, are presently the main source of ^{129}I in the environment. The ^{129}I concentration in environmental samples has increased 3–8 orders of magnitude compared with pre-nuclear era level, and reached to 10^{-10} to 10^{-4} for $^{129}\text{I}/^{127}\text{I}$ ratio. Despite the importance of ^{129}I speciation not only in radiation protection related to high mobility of iodine in nuclear waste depository and the environment and possible high bioavailability and concentration in human thyroid, but also in its application as an environmental tracer, the data are scarce. It is, therefore, the understanding of ^{129}I speciation in the environment represents a vital tool for tracing transport mechanisms, distribution pathways and bioavailability in the environment. To achieve that, specific chemical extraction methods and high sensitivity analytical techniques have been developed recently. The reported works on ^{129}I speciation mainly focus on water and atmosphere, and fractionation of ^{129}I in soil and sediment. The methods used for speciation

analysis of ^{129}I in water sample are based on anion exchange chromatography, and aimed for the determination of iodide, iodate and organically associated iodine. ^{129}I speciation in seawater has shown potential tracer capability of sources. The method used for speciation of ^{129}I in the atmosphere is based on trapping of different species by several filters, which separate ^{129}I in three fractions, particle associated, inorganic gaseous and organic gaseous iodine. A few data have shown that speciation of ^{129}I in atmosphere can supply useful information about the source and transfer pathway. The sequential extraction methods, normally used for various components of soil and sediment, have provided information about the water-soluble, exchangeable, carbonate, oxides, organic and mineral associated ^{129}I . Some of the results have indicated different fractionation pathways for ^{129}I and ^{127}I . Until now there are no published data about the speciation of ^{129}I in biological samples.

The bioavailability of ^{129}I is expected to be strongly dependent on its speciation, where iodide and iodate have a higher bioavailability (uptake by plants and animals) than the fraction associated with organic matters. The radiation toxicity of ^{129}I is relatively insignificant as the effective radiation dose to the thyroid is only about $1\ \mu\text{Sv}\cdot\text{y}^{-1}$ at the present environmental level ($^{129}\text{I}/^{127}\text{I}$ of 10^{-6}). This is 1000 times lower than the radiation dose from the natural background radiation ($1\ \text{mSv}\cdot\text{y}^{-1}$). Even in the heavily contaminated areas ($^{129}\text{I}/^{127}\text{I}$ of 10^{-4}), the radiation dose ($0.1\ \text{mSv}\cdot\text{y}^{-1}$) is still 10 times lower than the dose from the nature background, and 2 times lower than the dose from natural ^{40}K in human body.

Acknowledgements

Authors (X.L. Hou and V. Hansen) thank Villum Kann Rasmussen Foundation for financial support. The authors also wish to thank the NKS-B programme for support of the SPECIATION project, which provided possibilities for cooperation of the authors from Nordic countries on this article.

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Paper II

Yi P, Aldahan A, Hansen V, Possnert G, Hou XL. Iodine Isotopes (^{129}I and ^{127}I) in the Baltic proper, Kattegat and Skagerrak Basins. *Environ. Sci. Technol.* 2011, 45, 903-909

Iodine Isotopes (^{129}I and ^{127}I) in the Baltic Proper, Kattegat, and Skagerrak Basins

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Received August 19, 2010. Revised manuscript received December 5, 2010. Accepted December 9, 2010.

Radioactive anthropogenic pollution has raised concerns about the present and future environmental status of the semienclosed Baltic Sea. We here study the distribution and inventory of the anthropogenic radioactive ^{129}I in water depth profiles collected from 16 sites in August 2006 and 19 sites in April 2007 in the Baltic Proper and related Kattegat and Skagerrak basins. The results reveal considerable differences of ^{129}I concentration in terms of spatial and temporal variability and expose relatively high concentrations in the deep waters. Variability in the concentration of ^{127}I , stable natural isotope of iodine, seems to follow changes in the seawater salinity, but in oxygen-poor bottom waters sediment diagenetic release may contribute to the concentration of both isotopes in the water body. Inventory estimates show that ^{129}I in August 2006 (24.2 ± 15.4 kg) is higher than that in April 2007 (14.4 ± 8.3 kg) within the southern and central Baltic Proper whereas almost a constant load occurs in the Kattegat Basin. Calculated model inventory shows correspondence to empirical data and provides a guideline for future environmental assessment on the impact of ^{129}I load in the studied region.

Introduction

The semienclosed Baltic Sea and its ecosystem, surrounded by nine countries and a set of metropolitan areas, greatly affects the economic and recreational situations for more than 80 million people inhabiting its coasts and within its catchment area. However, since the early 1960s, accelerated industrialization and exploitations of natural resources pose a threat to the state of the Baltic Sea environment, such as eutrophication, overfishing, and toxic contaminants. Recent concern over the environmental conditions in the Baltic Sea has derived many governmental agencies and scientists to focus their research on defining the magnitude of the problems and providing suggestions for remedial measures. Among the many pollutants in the Baltic Sea, the anthro-

pogenic concentrations of radioactive ^{129}I ($T_{1/2} = 15.7$ Myr) were reported to be voluminous and far exceeding natural abundance (1). ^{129}I concentration in recent environmental samples is 3–8 orders of magnitude higher than pre-nuclear era level (2). Discharges from the two nuclear fuel reprocessing plants at La Hague (France) and Sellafield (UK) represent the major source contributing to ^{129}I in the North Sea (1, 3), and the Baltic Sea is largely overwhelmed by this source.

Iodine is an essential element for human, as indispensable gradient for the thyroid gland and many tissues normally bound with proteins (4). Thus, systematic and extensive data are necessary in order to understand the level of anthropogenic isotope in natural environment, future changes, and expected environmental hazards. Although a couple of studies raise the awareness, detail samplings that cover the spatial distribution of the isotope in the Baltic Sea are poorly defined. As most of the previous studies were restricted to sporadic samples and surface water (1–3, 5, 6), the distribution patterns and inventory of ^{129}I in the Baltic Sea have never been systematically estimated. In addition to direct environmental impact, a better understanding of the isotope distribution and sources in the Baltic Sea provide possibility of utilizing the isotopes as an oceanographic tracer (2).

Although about 5500 kg have been released to the environment since the atomic era, it is estimated that around 70 000 kg of ^{129}I is still pending in unprocessed nuclear fuel (7). Such huge amount of ^{129}I will further address our concerns. As continuous monitoring is time-consuming and expensive, model simulation could instead be a useful tool for future inventory prediction.

Another significant aspect of iodine distribution in the marine environment is that iodine primarily exhibits two main oxidation states as iodide (I^-) and iodate (IO_3^-) and minor organic iodine (8). Given different oxygen condition prevailing in the Baltic Sea, distribution of the iodine isotopes may depend on the extent of changes between oxic and anoxic water. Although iodine is highly soluble chemically, the biophilic nature of iodine tends to enrich the element in the organic fraction (8). Characterized by seasonal variations, the changeable conditions (like quantity of renewed water budget, temperature, organic productivity) in the Baltic Sea may therefore induce relative changes in concentrations of ^{129}I . To our best knowledge, seasonal monitoring has not been carried out for iodine isotopes.

Although the earlier data about iodine (either as ^{129}I or ^{127}I) variability in the Baltic Sea and Skagerrak basin provide some guidelines about the isotopes distribution, there is a lack of systematic depth profile data in term of sampling period and a contemporaneous analysis of both isotopes in the samples. This situation made interpretation of the isotopes, and particular ^{129}I variability and inventory in water bodies highly speculative and thereby the environmental significance of ^{129}I and future predictions. Despite the possibility that the isotope may not be a source of immediate environmental hazard, comprehensive understanding of present situation and prediction of future changes are indispensable for the region.

We here present extensive data on depth profiles of ^{129}I and ^{127}I during two seasons represented by the months of August 2006 and April 2007 in the Baltic Proper and the Skagerrak-Kattegat basin. The data are used, together with other relevant information such oxygen concentration, salinity and temperature, to reveal the magnitude of variability in the iodine isotopes during, early spring (huge influx of fresh water and enhanced thermohaline circulation) and late summer (extensive algal blooming and relatively maxi-

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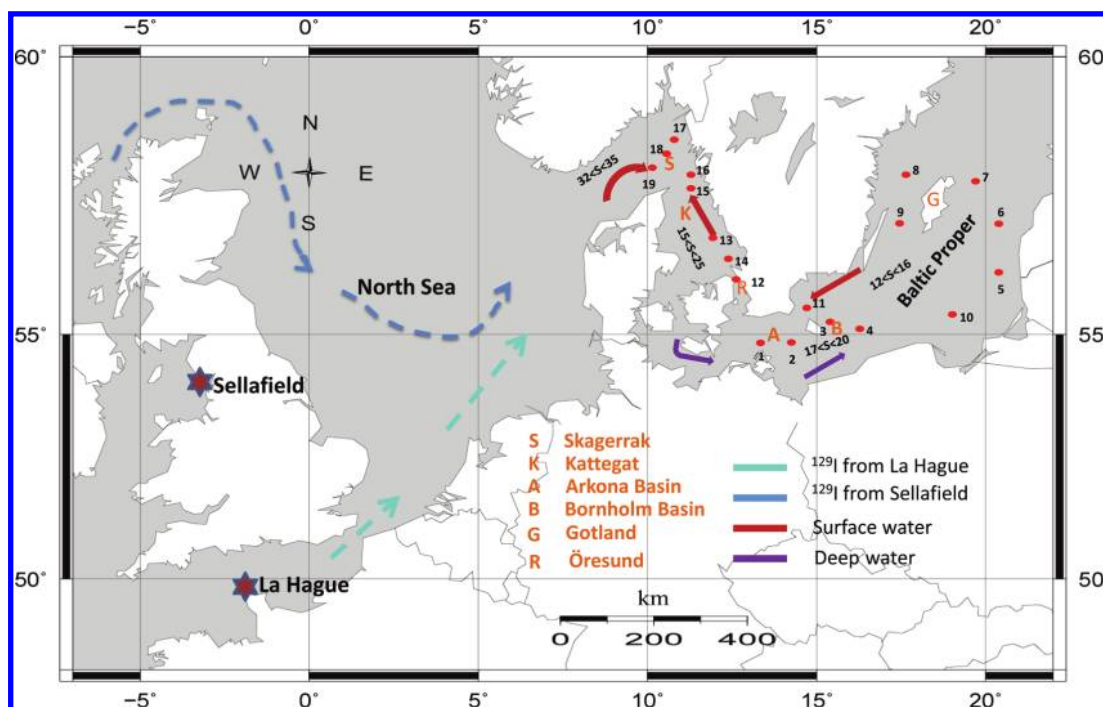


FIGURE 1. Sampling sites (the red solid circle) for August 2006 and April 2007 expeditions. Blue and turquoise arrows represent ^{129}I transported from Sellafield and La Hague, respectively. Purple arrows refer to deep flow into the Baltic Proper while red arrows mean surface flow. Ranges of salinity concentration, within the Skagerrak, Kattegat, and Baltic Proper, are labeled.

mized stratification). Furthermore, inventory estimates are updated and a model is developed for future prediction, involving the processes of seawater inflow and outflow, freshwater tributary and sedimentation effects.

Sampling and Analytical Techniques

Depth-profiles of seawaters were collected from 16 sites in August 2006 and 19 sites in April 2007 (Figure 1 and Supporting Information Figure S-1). Sampling was carried out by the research Vessel Argos, operated by the marine division of the Swedish Meteorological and Hydrological Institute. Water samples from different depths were collected in Nansen bottles (Hydro Bios). Meanwhile, a CTD automatic sampler (CTD- model SD204) was launched to measure hydrologic parameters such as salinity, temperature, depth, and dissolved oxygen. Salinity was also measured on board, using an AEG MINISAL 2100 salinometer based on relative conductivity. Oxygen was determined by Winkler titration method using an automated potentiometric titration system and detail of the procedure has been reported elsewhere (9).

Iodine isotopes were extracted from seawater by following the method of Hou et al. (10, 11), and the details are presented in the Supporting Information. To all samples, 0.2 mL of 200 Bq/mL $^{125}\text{I}^-$ (NaI) as a chemical yield tracer and 2.0 mg of stable iodine (Woodward Iodine Company, U.S.) as a carrier were used. Iodine species were separated by anion exchange chromatography and determination of ^{129}I and ^{127}I were carried out using Pelletron (NEC machine) AMS and an X Series^{II} ICP-MS (Thermal Electron Corporation), under hot plasma conditions, with the Xt interface system. Processing blanks $^{129}\text{I}/^{127}\text{I}$ value was $1.5 \pm 0.5 \times 10^{-13}$, which is more than 2 orders of magnitude lower than the value in the samples. Total analytical uncertainty for $^{129}\text{I}/^{127}\text{I}$ value is normally less than 10% and the detection limit for ^{127}I , calculated as 3SD of blanks, was 0.27 nM.

Results

The data sets of ^{127}I and ^{129}I together with temperature, oxygen concentration and salinity for the two sampling campaigns

of August 2006 and April 2007 are presented in Supporting Information Tables S-1 and S-2 and Figures S-2 and S-3. Surface and deep water (above and below halocline, respectively) distributions of the isotopes and their ratio indicate several differences as shown by Figures 2 and 3. In both August 2006 and April 2007, surface water ^{129}I concentration (Figures 2a and 3a) have their highest values in the Skagerrak basin with a maximum reaching up to 1683×10^8 atoms/L (or 106×10^{-8} for $^{129}\text{I}/^{127}\text{I}$ atomic ratio). The trend of concentration decreases toward the Öresund (location 12), and remains rather constant, around $25\text{--}36 \times 10^8$ atoms/L, in the Baltic Proper. Relatively more variable distribution of ^{129}I between the two sampling times is revealed by the concentration in the deep water (Figures 2b and 3b). The plume of maxima shown in the Skagerrak during August 2006 is partly retained along the Swedish coasts during April 2007. Relatively high concentrations are also retained throughout the Arkona basin during April, but the more homogeneous distribution in the southern and central parts of the Baltic Proper during April is disturbed by an increase along the Bornholm deep.

To summarize the ^{129}I depth distribution, we observe a 2–19 times decrease in concentration from the surface down to bottom layer in the transition zone between the Kattegat and Skagerrak (locations 17–19, Figure 4). While in the Kattegat (locations 12–16), ^{129}I concentration gradually increases with depth above halocline, around 35 m, whereas the opposite trend is observed below 35 m. In the Arkona basin (locations 1 and 2, Figures 2a, b and 3a,b), a rather sensitive region for different seasons, high ^{129}I concentrations are observed in August 2006 in the surface layer, extending to around 30 m, and then the concentration decreases with increasing depth. But an opposite trend was found in April 2007 where ^{129}I concentration increased from the surface water ($33 \times 10^8 \pm 3$ atoms/L) to the bottom water ($163 \times 10^8 \pm 27$ atoms/L). In the central Baltic Proper (locations 5–10), there is an obvious ^{129}I stratified layer where the concentration increases with depth and attains a maximal value 150×10^8 atoms/L in the bottom water in August 2006.

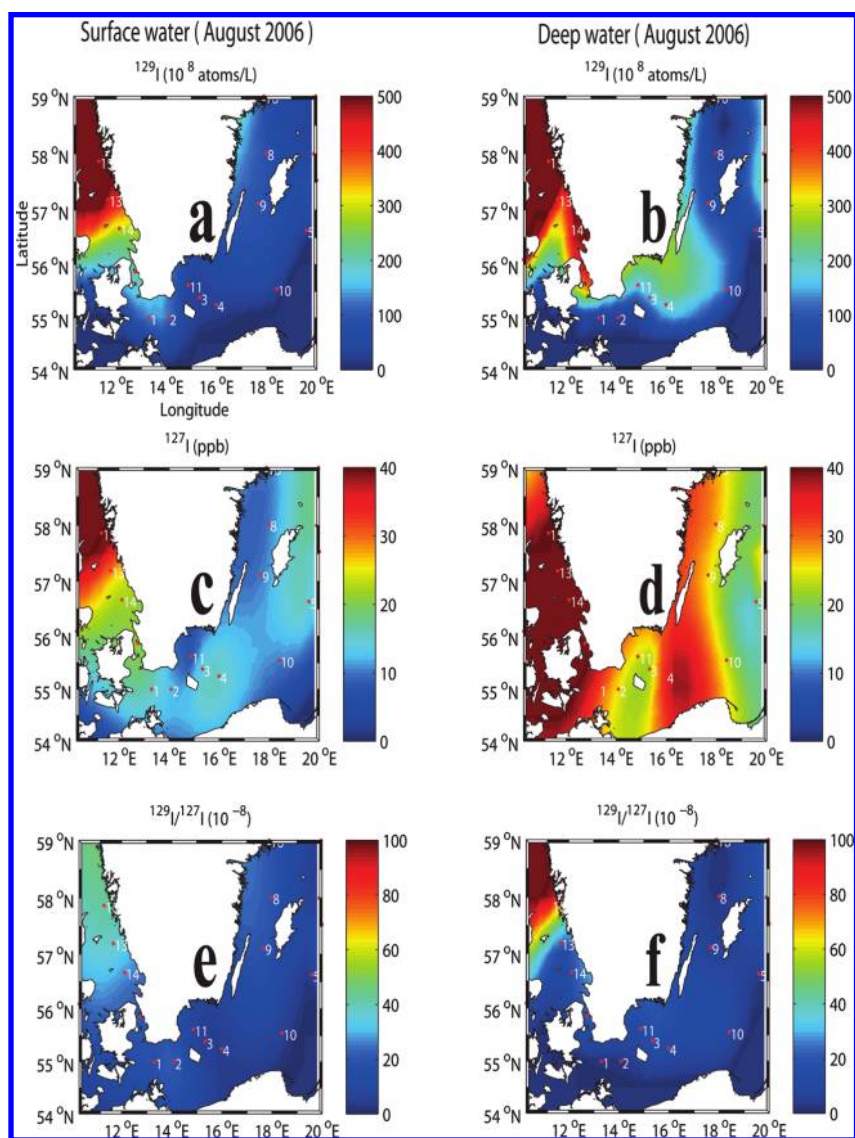


FIGURE 2. Horizontal distribution of ^{129}I , ^{127}I , $^{129}\text{I}/^{127}\text{I}$ in surface and deep waters of August 2006.

Distribution of ^{127}I in the surface waters (Figures 2c and 3c) shows decreasing trends from maximum value in the Skagerrak-Kattegat, 40 ppb in August 2006 and 30 ppb in April 2007, to the Baltic Proper, average value of 12 ± 4 ppb. Similar to ^{129}I , surface waters from sites 13 and 14 near to the Öresund still show the highest ^{127}I values in the bottom layer for the two seasons with an average of 48 ppb (Figures 2d and 3d). In the deep waters distribution of ^{127}I is rather different during the two sampling campaign, where strips of high concentrations, up to 35 ppb in August 2006, occur in the Baltic Proper (Figures 2d and 3d). In general, the vertical distribution of stable iodine (Supporting Information Figures S-2c, 2d, 3c, and 3d) in the two sampling periods follows more the pattern of salinity ($R^2 = 0.85$) in August 2006 compared with April 2007 ($R^2 = 0.54$). In the Kattegat and Skagerrak basins the values rise from 30 ± 5 ppb in the surface water to 45 ± 9 ppb in the deep water, while a gradient is also found in the Baltic Proper, particularly during August 2006, but at a lower magnitude (from 12 ± 4 ppb in surface water to 18 ± 7 ppb in bottom water).

A rather smooth transition ($50\text{--}20 \times 10^{-8}$) is found in the ratio of $^{129}\text{I}/^{127}\text{I}$ surface water moving from the Skagerrak to Kattegat in the August 2006 data set (Figure 2e). In the data set of April 2007, an abrupt decline (from 100 to 11×10^{-8}) appears in the surface water along the same pathway (Figure 3e). In the Baltic Proper, $^{129}\text{I}/^{127}\text{I}$ of surface waters present a

wide range ($3\text{--}22 \times 10^{-8}$) in August but more homogeneous in April ($7 \pm 2 \times 10^{-8}$, Figure 2e and e). The situation in the deep water indicates iodine ratio normally around 18×10^{-8} in the Kattegat during the two seasons (Figures 2f and 3f). In the Baltic Proper, the $^{129}\text{I}/^{127}\text{I}$ value seems to be uniformly distributed in the surface and deep water in both August and April data where a gradually increase with depth from 5×10^{-8} to 14×10^{-8} in August and 6×10^{-8} to 15×10^{-8} in April is found.

Salinity distribution is rather similar in August and April data sets which show a sharp declining plume from Skagerrak Basin (32–35) toward the southern Baltic and a decrease to 17–20 in the Arkona Basin and to 12–16 in the Baltic Proper. A halocline at around 75 m occurs above the deep water with average salinity of 10 in the Baltic Proper. Seasonal variability causes a contrasting effect on temperature depth profile in the Baltic Sea, which appears nearly uniform in April down to one hundred meter depth, whereas a distinct gradient emerges in August, typically descending from 17°C in the surface to 5°C in the bottom water. Dissolved oxygen concentration in the surface water of the Baltic proper is higher by 2.0 mL/L in April compared with that in August. Anoxic conditions, with oxygen concentration commonly less than 2.0 mL/L, were detected in the bottom water of Baltic Proper, especially in the East Gotland Deep.

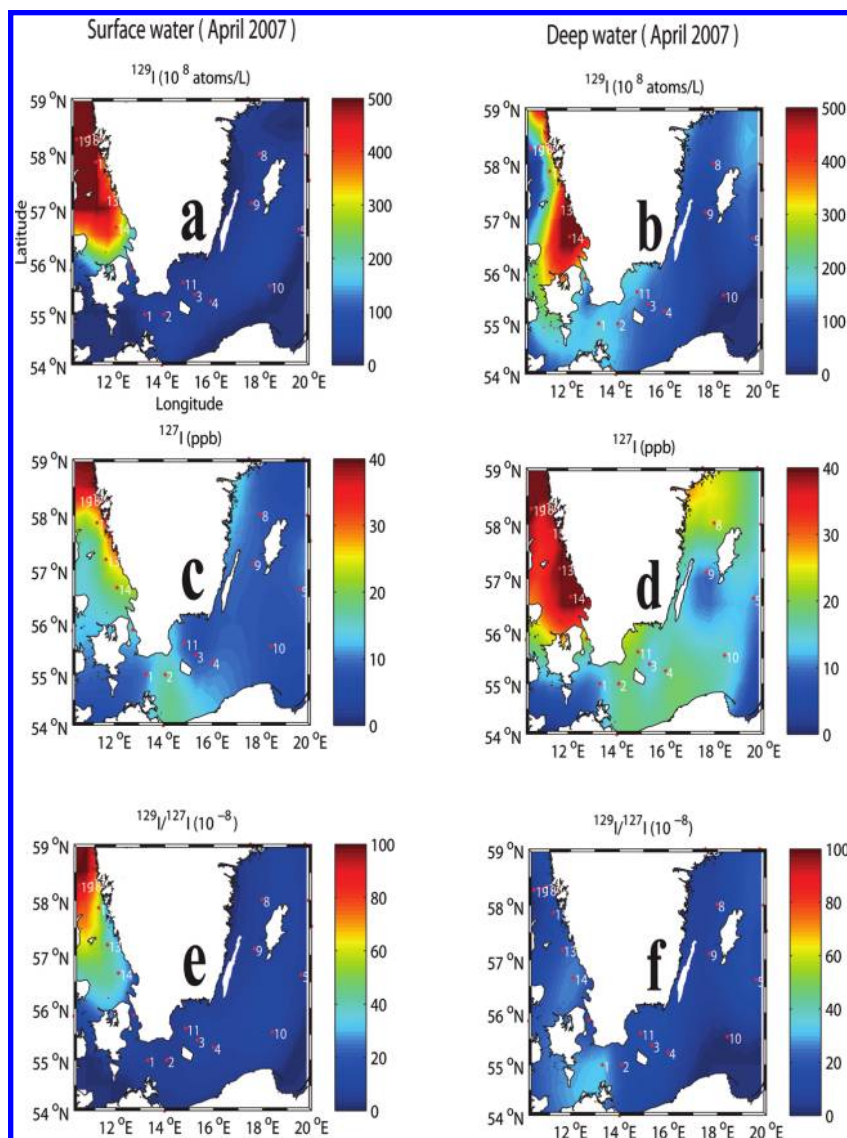


FIGURE 3. Horizontal distribution of ^{129}I , ^{127}I , $^{129}\text{I}/^{127}\text{I}$ in surface and deep waters of April 2007.

Details of the depth variability in the $^{129}\text{I}/^{127}\text{I}$ values, salinity and oxygen are presented in the Supporting Information (Tables S1 and S2 and Figures S1–S4).

Discussion

Water Masses and Sources of Iodine Isotopes in the Skagerrak-Kattegat. The Skagerrak water masses (Figure 1) represent (1) outflow of low salinity surface water from the Kattegat; (2) inflows of high salinity (34–35) surface water from the North Sea, and (3) inflow of high salinity deep Atlantic water (>35) (15, 16). The similar ^{129}I level in the Skagerrak surface water reported here and that reported value in coastal water in Jutland (2) suggests that a large portion of ^{129}I pool in the Skagerrak is contributed from the Jutland currents. ^{129}I concentration decreases to about 4×10^{10} atoms/L in intermediate layer water with salinity about 33. We suggest that this water mass represents dilution of surface North Sea water by low salinity and outflow Kattegat water, which is illustrated by the sharp ^{129}I concentration plume observed from 10.8°E to 12°E during April 2007. Extremely low ^{129}I concentration (9×10^9 atoms/L) and $^{129}\text{I}/^{127}\text{I}$ value (average 4×10^{-8}) was measured in the bottom water of Skagerrak with salinity over 35, whereas ^{127}I concentration corresponds to the high salinity seawater. This feature is, therefore, attributed to existence of ^{129}I poor Atlantic water,

which is also confirmed by a similar $^{129}\text{I}/^{127}\text{I}$ value ($\times 10^{-8}$) reported in water collected in the northern North Sea (2, 6).

In the upper water layer of the Kattegat (above halocline at around 35 m) (Figures 2a and 3a), ^{129}I concentration decreases from north (location 15) to south (location 13), and increases with depths. This trend is also imprinted in the correlation between ^{129}I and salinity ($R^2 = 0.57$ in August 2006 and 0.92 in April 2007) and the range of salinity (from 19 to 33) that is less than bottom water of Skagerrak (>35). Such pattern indicates that the ^{129}I pool in the Kattegat represents a mixture of three water masses, namely surface and intermediate water of Skagerrak and outflow low salinity Baltic Proper water via the Öresund.

In the deep water (below 35 m) of the Kattegat (Figures 2b and 3b), ^{129}I decreases with depth, and is negatively correlated with the salinity ($R^2 = -0.54$ in August 2006 and -0.19 in April 2007). This behavior suggests mixing of the intermediate and deep waters in the Skagerrak as a source of ^{129}I to bottom water of the Kattegat. In addition, the gradually decreasing ^{129}I level to the south of Kattegat can also be attributed to this gradually blending process with less ^{129}I outflow water from the Baltic Sea. Furthermore, such trend seems less obvious in the waters collected in August 2006 than in April 2007. An explanation can be a more active mixing process in August and possible increased incorpora-

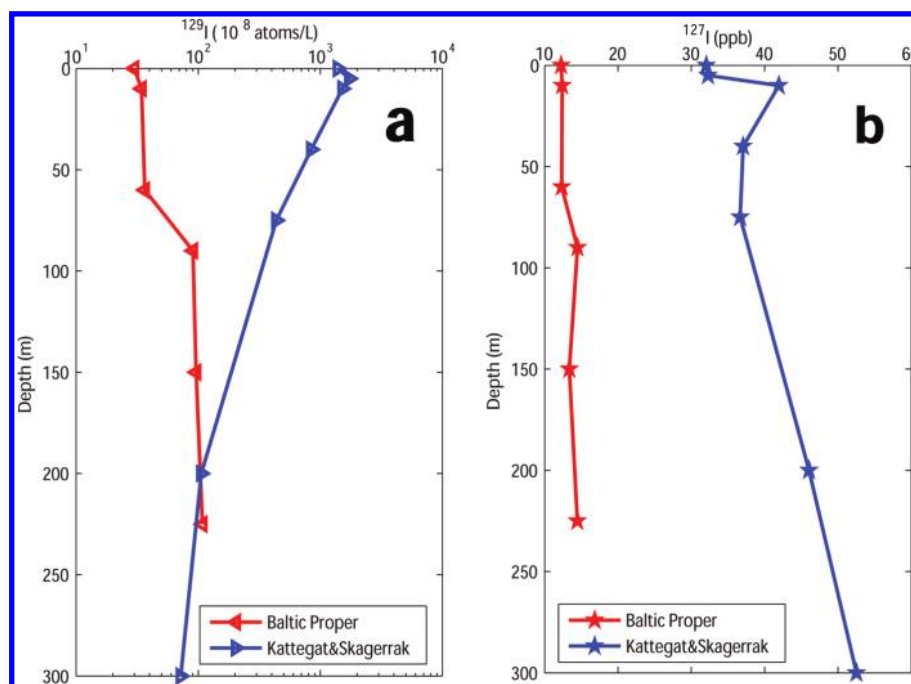


FIGURE 4. Typical depth distribution of ^{129}I (a) and ^{127}I (b) in the Baltic Proper site 6 (red line) and the Skagerrak-Kattegat site 19 (blue line).

tion of iodine in biological particles associated with extensive algal blooming. This process would speed up homogenization of water masses and thereby reduces difference in ^{129}I concentration.

Distribution of phosphate concentration in the same geographic scales as iodine isotopes was obtained from WORLD OCEAN DATABASE (<http://www.nodc.noaa.gov>) (Supporting Information Figure S-6). Although the two elements (phosphorus and iodine) have different sources to the studied water basins, the geochemical behavior (17) is rather similar and may shed light on the distribution patterns. Transect of phosphate from Kattegat to the southern Baltic Proper (from 12° E to 16° E) shows similar response to that described for iodine, increasing with depths and a maximum value in the bottom layer. Despite different sources for the two elements (P and I), their distribution in the Kattegat seems comparable where the seawater-dilution process has preferentially influenced both elements.

Water Masses and Sources of Iodine Isotopes in the Baltic Proper. A significant decrease of ^{129}I (and also ^{127}I) concentration in surface waters from the Kattegat ($>500 \times 10^8$ atoms/L) through the Öresund (217×10^8 atoms/L in August, 82×10^8 atoms/L in April) to southern Baltic Proper (average 136×10^8 atoms/L in August, 37×10^8 atoms/L in April) is clearly illustrated during the two sampling campaign (Figures 2a, c and 3a, c). This pattern also agrees with previous observations (1, 3, 6). In the surface water of the Baltic Proper, the iodine concentrations apparently show more relative changes during August than April that may relate to active algal blooming during August.

^{129}I concentration in the deeper water shows considerable variability that can be linked to both magnitude of water influx and water residence time. The bottom waters in the Gotland deep, the deepest part in the Baltic Proper, reside for a long time (5–10 years) in anoxia and hypoxia conditions and could be only displaced by the rarely occurred “major Baltic inflows” with salinity over 17 (18, 19). There are some extreme high values of ^{129}I in waters with relatively low salinity (below 13) in the Gotland deep. This feature could not be merely explained by effect of only saline water intrusion. The average oxygen concentration of the deep water in this area is <2 mol/L and such oxygen-depleted condition can

mobilize iodine associated in sediments to aquatic phase by diagenetic processes (20). The difference of iodine concentration between the two seasons in the Eastern Gotland deep may be related to upwelling resulting from temperature difference between the surface (range at 16 – 21°C) and the deep waters (4 – 6°C) (21). Apparently, waters enriched in iodine originating from sediment diagenetic release were not fully upwelled to the surface. Instead these waters are restricted to depths below 75 m where the halocline may hamper water exchange between surface and deep layers. Anoxic condition (<2 mL/L oxygen concentration, locations 5–7) in the Gotland Deep is also reflected by the vertical distribution of phosphorus that shows an evident gradient from surface to deep layers below halocline. It is suggested that sediments act as “sinks” for phosphorus under oxic conditions and act as “source” during hypoxic situations (19, 22). This pattern strongly resembles iodine distribution in both August 2006 and April 2007 and it further confirms ^{129}I source from sediment diagenetic release.

Similar to ^{129}I , extensive ^{127}I diagenetic release from sediment in the Baltic Proper under anoxic environment can also be the reason for high values in the bottom water (Figures 2d and 3d). In the Baltic Proper, ratio of $^{129}\text{I}/^{127}\text{I}$ maintains similar pattern in August and April and tends to be less diverse. This behavior suggests that both isotopes are affected by local conditions, with respect to influence of the ecosystem through anoxia, sediment water exchange, and biological processes. To clearly separate these effects, speciation analysis of the isotopes would provide vital information for future research.

Comparison with Earlier Results. Data of ^{129}I from the present study and those from comparable sites measured in previous investigations (Supporting Information Table S-3) are plotted for the Skagerrak, Kattegat and Baltic Proper (Figure 5). Surface waters with average ^{129}I concentration of 11×10^8 atoms/L in the East Gotland (near to sites 6 and 7) collected in 1999 (6, 12), were nearly six and two times less than those values from August in 2006 and April in 2007 reported here. In the Kattegat, concentration of ^{129}I in the two years of 2006 and 2007 were also higher (500×10^8 atoms/L) than the value of (300×10^8 atoms/L) reported around the

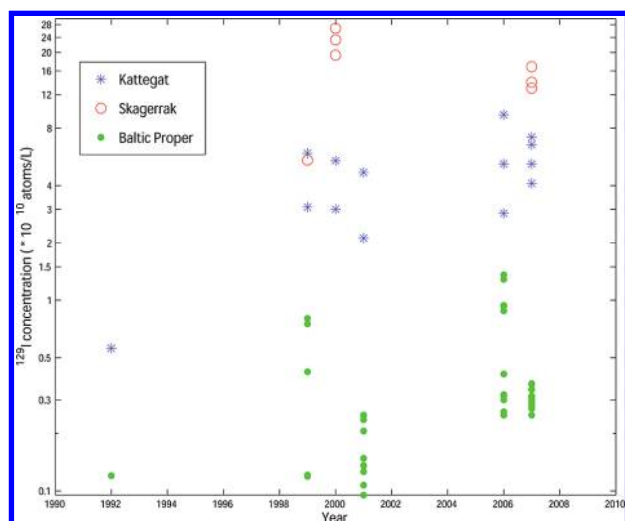


FIGURE 5. Time series data of ^{129}I concentration in the Skagerrak (red circle), Kattegat (blue star) and Baltic Proper (green dot) based on results from this study (2006 and 2007) and published data from 1992 to 2001 listed in Supporting Information Table S-3.

year of 2000 and even much higher than the value (56×10^8 atoms/L) in 1992 (5).

Influence of the release function from the reprocessing facilities on the distribution of ^{129}I in the studied region with time is captured through constructing a delayed arrival response. Transit time for the radioactive plume from Sellafield and La Hague to the Baltic Sea was intensively discussed (3, 13, 14) and the estimate varies in different literatures. We have set, arbitrarily, a 3 year delay for ^{129}I discharged from Sellafield and 2 years from La Hague to arrive at the Baltic Proper and calculated the delayed release function (details presented in the Supporting Information Figure S-5). The pattern of marine discharges function agrees well with the ^{129}I time series in the Skagerrak. The relatively strong increase in the discharge between 1992 and 2002 is manifested in the measurements reported from Skagerrak and also in the Kattegat and Baltic Proper. The year of 2000 represents a turning point in the Kattegat and in the Baltic Proper. Owing to long period of water stagnation, in particular deep portions of the Kattegat and Baltic Proper, ^{129}I may accumulate and thus the response to the discharge function would be sluggish and not scaled to the release function.

^{129}I Inventory Estimation. Published data on ^{129}I inventory in the Baltic Sea were sparse, averaged for the whole water mass and scaled to the year of 2001 at that time (1, 6). Here we update the inventory estimation based on our data set, where contribution from each water mass is calculated by averaging ^{129}I concentration from different layers, multiplying by the corresponding water volumes in each basin. The results show that the inventory of ^{129}I in August 2006 (24.2 ± 15.4 kg) is much higher than that in April 2007 (14.4 ± 8.3 kg) within the Baltic Proper. In the Kattegat, a similar inventory of ^{129}I for August (5.5 ± 1.8 kg) and April (5.1 ± 3.8 kg) was obtained. The estimated inventory of ^{129}I in the Skagerrak reservoir is 11.4 ± 0.4 kg, in which over 80% resides in the surface and intermediate layers.

A simplified calculation is set up to simulate ^{129}I inventory in the Baltic Proper based on the assumption that the source of ^{129}I in the Kattegat is only attributed to Sellafield and La Hague marine discharges (for the detailed model see Supporting Information Table S-4 and Figures S-5, S7, and S9). ^{129}I input from fresh water system such as rivers and precipitation and ^{129}I sink for sediment were also estimated. The natural inventory of 3.2×10^{-4} kg for the Baltic Sea (3) was adapted into the model as initial value and was run from

1968 to 2006 as liquid emission from Sellafield nuclear reprocessing facility was insignificant during the period of 1952–1965.

The modeled result shows that there has been 21 kg ^{129}I in the Baltic Proper by 2006 as liquid form and 1 kg trapped in the sediment. The estimates are rough because the few number of ^{129}I data and large variability in the Kattegat water body. Although effect of water and air exchange, mixing and diffusion were ignored in the model simulation, the results provide inventory approximations that can be helpful for future prediction by prolonging time series of input condition. A relatively large error (up to 60%) is expected to associate the simulated inventory of ^{129}I and the impact on adapting such estimate in radioactive risk assessments is marginal. This is because the isotope bioavailability and transport between the different ecological compartments (water, sediment, and biota) are still poorly investigated. Furthermore, extensive anoxia conditions and disturbance of the thermohaline and the water mass layering can be potential processes associating a future global warming effect on the region. Development of such new conditions in the Baltic Sea is predicted to enhance releases of iodine bound in the sediment and most likely the load of the ^{129}I in the water column. Therefore, further evaluation of bioavailability of the isotope in the ecosystem is indispensable for a sustainable future environmental assessment and risk management impact in the region.

Acknowledgments

The authors thank Lars Andersson and Bodil Thorstensson and all the crew and scientific team on board of the research vessel Argos for the help during the sampling expeditions. Funding for the sampling was provided by the Swedish Meteorological and Hydrological Institute (SMHI) and for the analyses by the Tandem Laboratory, Uppsala University. X.L.Hou appreciates the support by “BaiRen” Project of CAS (Grant No. KZCX2-YW-BR-13).

Supporting Information Available

Description of chemical separation and measurement for ^{129}I and ^{127}I , data plotting and model parameters with nine figures and four tables as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ES102837P

Iodine Isotopes (^{129}I and ^{127}I) in the Baltic Proper, Kattegat and Skagerrak Basins

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Prepared date: 2011-12-05

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This supporting information consists of 6 text pages describing chemical separation and measurement for ^{129}I and ^{127}I , data plotting and model simulation and 9 figures (S1-S9) and 4 tables (S1-S4).

Methods

Chemical separation and measurement

All water samples used for iodine isotopes analyses, were passed through a 0.45 μ m membrane filter and stored in cold and dark room until analysis. The extraction of iodine from seawater was based on the method by (1-2). 20 ml seawater was taken to a separation funnel and 0.2 ml of 200 Bq/ml $^{125}\text{I}^-$ (NaI) as chemical yield tracer and 2.0 mg of stable iodine (Woodward Iodine Company, USA) as a carrier were added. After addition of 0.2 mL of 2.0 M NaHSO_3 , 3 M HNO_3 was added to adjust pH1-2 to convert all inorganic iodine to iodide, 10 ml CCl_4 and NaNO_2 were added to oxidize iodide to iodine, which was extracted to CCl_4 phase by shaking. The CCl_4 phase was separated and transferred to another separation funnel, 10 ml water and 0.1 ml of 0.1 M NaHSO_3 were added to back-extract iodine to water phase, and the extraction procedure was repeated. Finally, iodine (iodide) was precipitated as AgI by adding AgNO_3 . Blank samples were prepared in the same way as described above for the seawater samples. After drying, AgI precipitate was ground and mixed with niobium, which was then pressed into copper holder for ^{129}I measurement. ^{129}I was measured by AMS system (the Pelletron NEC machine) in Tandem Laboratory at Uppsala University using NIST SRM 4949C ^{129}I as a standard. The processing blanks $^{129}\text{I}/^{127}\text{I}$ values were $1.5 \pm 0.5 \times 10^{-13}$, which is more than 2 orders of magnitude lower than the value in the samples. Total analytical uncertainty for $^{129}\text{I}/^{127}\text{I}$ ratio is normally less than 10 %.

For the determination of ^{127}I from seawater, the samples were diluted for 20 times using 0.015 M NH_4OH and Cs^+ as (CsCl) was added as an internal standard to the concentration of 2.0 ng/ml. The concentration of iodine was measured using an X Series^{II} ICP-MS (Thermal Electron Corporation), under hot plasma conditions, with the Xt interface. Iodine standard solutions were

prepared using KI and KIO₃. No difference of signal intensity between Iodide and iodate was observed. The detection limit, calculated as 3SD, of blanks was 0.27 nM.

Data plotting

The depth distribution of ¹²⁹I was plotted using ODV (Ocean Data View) software, which is specific for graphical display of gridded data. VG Gridding algorithm was implemented to construct the rectangular grid and the same value 100 per mile was set for grid-spacing along X and Y directions. Concentrations of ¹²⁹I, ¹²⁷I, oxygen, salinity and ¹²⁹I/¹²⁷I for every grid point were calculated by a weighted-averaging scheme. This procedure allowed resolving dense data coverage area and at the same time provides acceptable representation for regions with sparse data.

Model description

The simple model used consists of four compartments, seawater inflow and outflow, freshwater tributary and sedimentation (Figure S-8). It is achieved on a yearly basis and performs from 1968 to 2006 as liquid emission from Sellafield nuclear reprocessing facility was insignificant during the period of 1952 to 1965. The natural inventory of 3.2×10^{-4} kg for the Baltic Sea (3) was adapted into the model as initial value and 10% analyzes error for iodine concentration is considered in the final results. The detail descriptions for each of dynamic process are illustrated in the following text.

Seawater inflow

¹²⁹I carried by seawater inflowing to the Baltic Sea has been estimated by using available historical concentrations in surface water of site 14 (Figure S-1) in the Kattegat as a function of accumulated mass of discharges from Sellafield and La Hague (Figure S-7). This relationship

produces a linear correlation with $R^2=0.81$ and we assume that the source of ^{129}I in the Kattegat is only attributed to Sellafield and La Hague marine discharges. The water exchange between the Baltic Sea and North Sea is largely influenced by meteorological and oceanographic conditions (4), but the annual seawater flux into the Baltic Sea has been averagely estimated to be 471 km^3 (5).

Seawater outflow

^{129}I flowing out of the Baltic Sea has been calculated by concentrations in the Baltic Proper multiplying by water outflow fluxes. Outflow of ^{129}I concentrations changes every computing time step with respect to ratio of inventory in the Baltic Proper to corresponding volume. In term of seawater flux out of the Baltic Sea, a constant value of 949 km^3 (5) has been averagely estimated.

Freshwater tributary

^{129}I tributary from fresh water system such as rivers and precipitation was also estimated and no consideration was given to groundwater inflow as ^{129}I content is expected to be insignificant (6). ^{129}I concentrations in the rivers surrounding the Baltic Sea is dominant by atmospheric deposition (7), and ^{129}I concentration is strongly latitude dependent in this area, with an average of $4.5 \times 10^8 \text{ atoms/L}$. This value is adopted in this model and the contribution from rivers is treated as a constant independent of time. The results show the insignificant rivers input to the Baltic Sea ^{129}I pool, which agrees with the estimation of Aldahan et al. (8). As annual average fluxes from precipitation (224 km^3) and evaporation (184 km^3) are nearly the same, thus the model used here does not account for the tributaries from them and assumes that magnitudes

of their contribution to the Baltic Proper are mutually counteracted.

Sedimentation

The sediment module, stressing on sediments-water exchange, as a source (9) may play significant role in simulation of ecosystems. In the model used here we have not distinguished between rocky and soft bottom, and a typically constant ^{129}I value of 22×10^8 atoms/g (10) and dry matter deposition flux within Baltic Sea (48×10^6 t/y, 11) are used. Then, based on the assumption that inventory is the same for every year, ^{129}I sink for sediment laden for 39 years is estimated.

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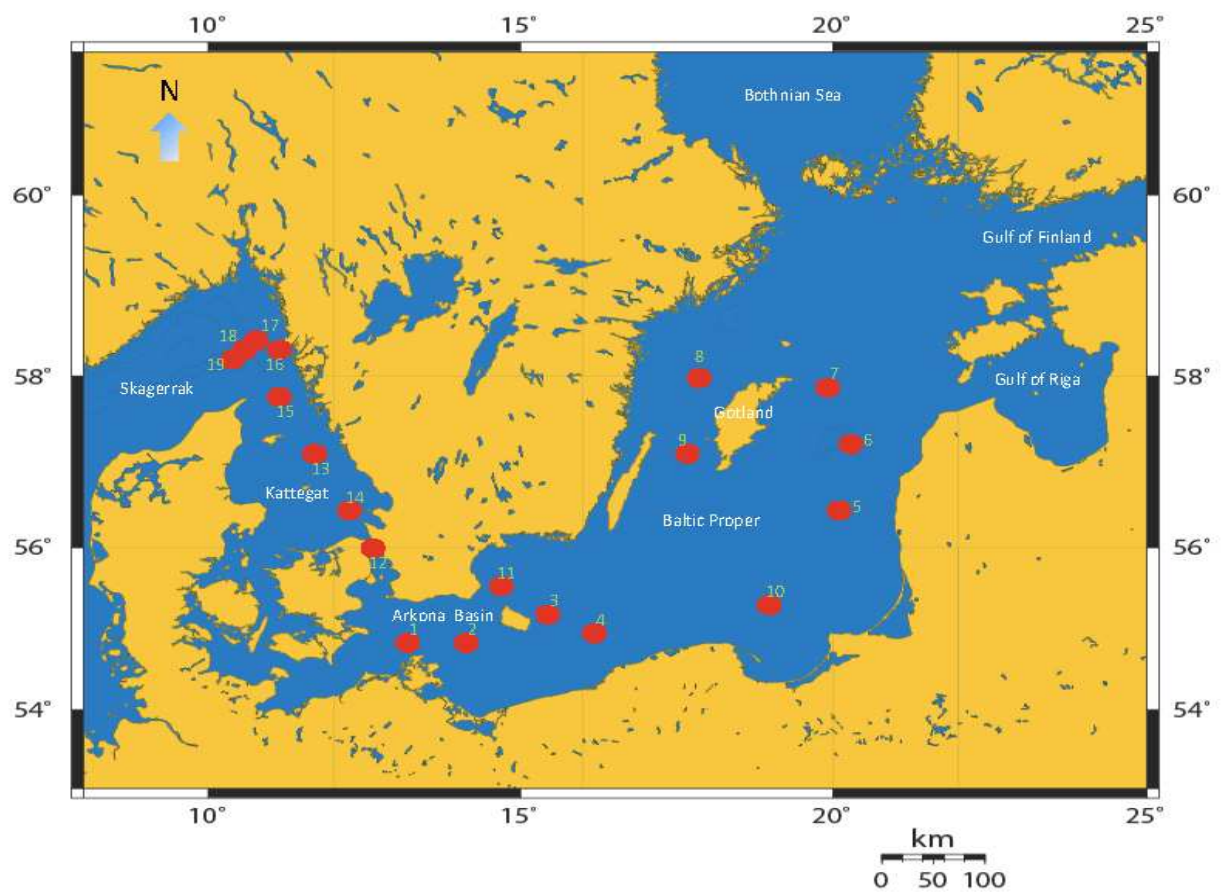


Fig. S-1 Sampling sites (the red solid circle) in the Baltic Proper, Kattegat and Skagerrak. Samples of August 2006 were collected from sites no. 1 to no. 16 and in April 2007 from sites no. 1 to no.19.

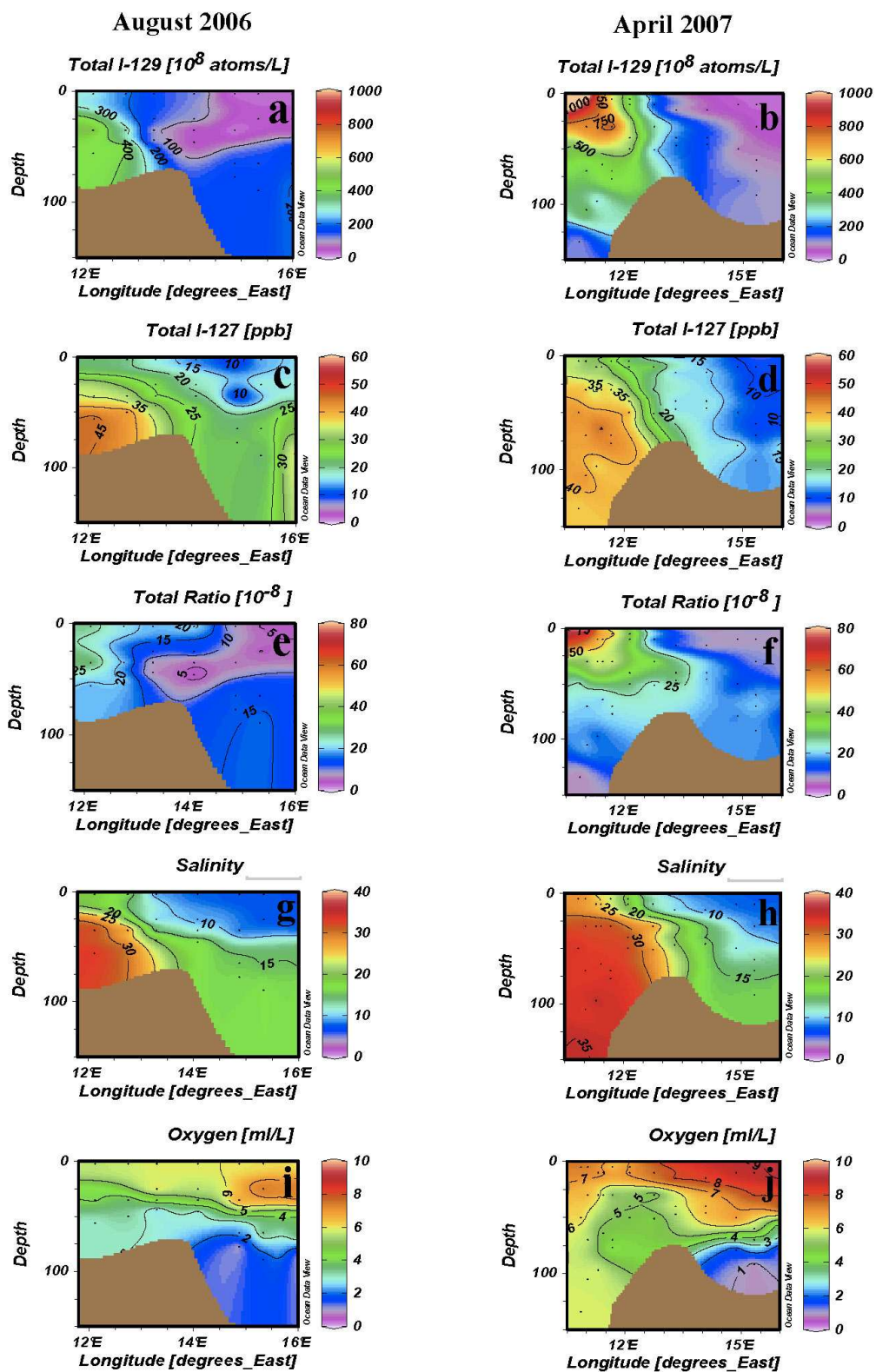


Fig. S-2 Vertical distribution of I-129, I-127, I-129/I-127, salinity and oxygen in the Skagerrak and Kattegat basins from August 2006 and April 2007

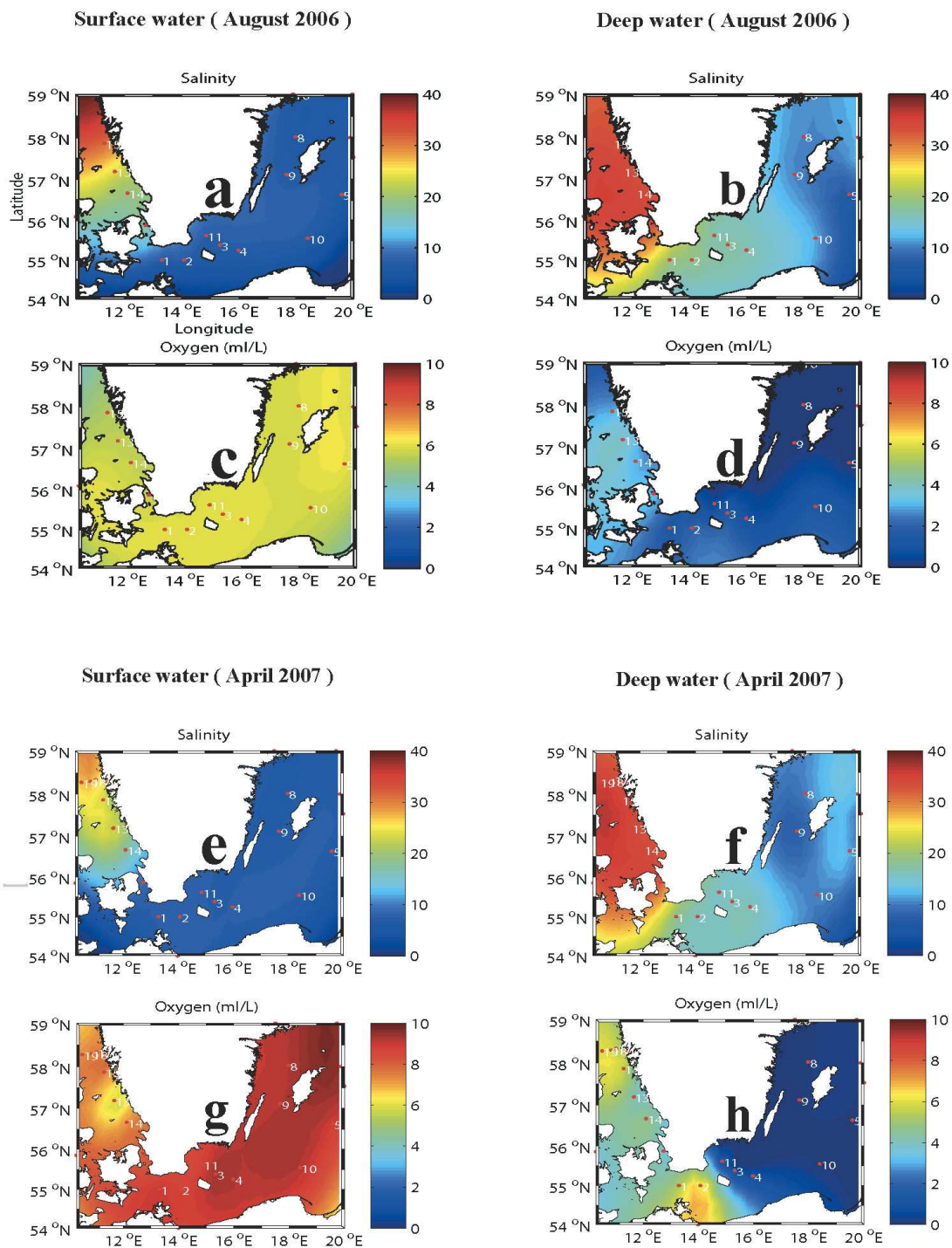


Fig. S-4 Horizontal distribution of salinity and oxygen in the Baltic Proper, Kattegat and Skagerrak from August 2006 (a-d) and April 2007 (e-h).

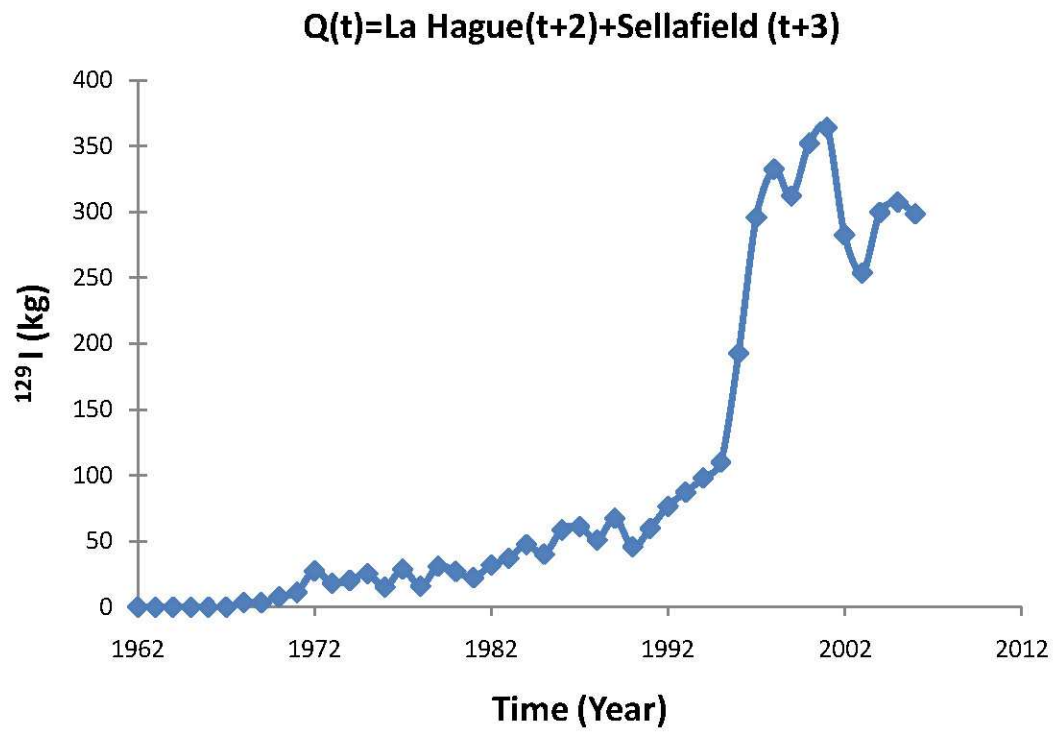


Fig. S-5 Marine discharges function (Q) for the total liquid release from the Sellafield and La Hague delayed with 3 and 2 years, respectively.

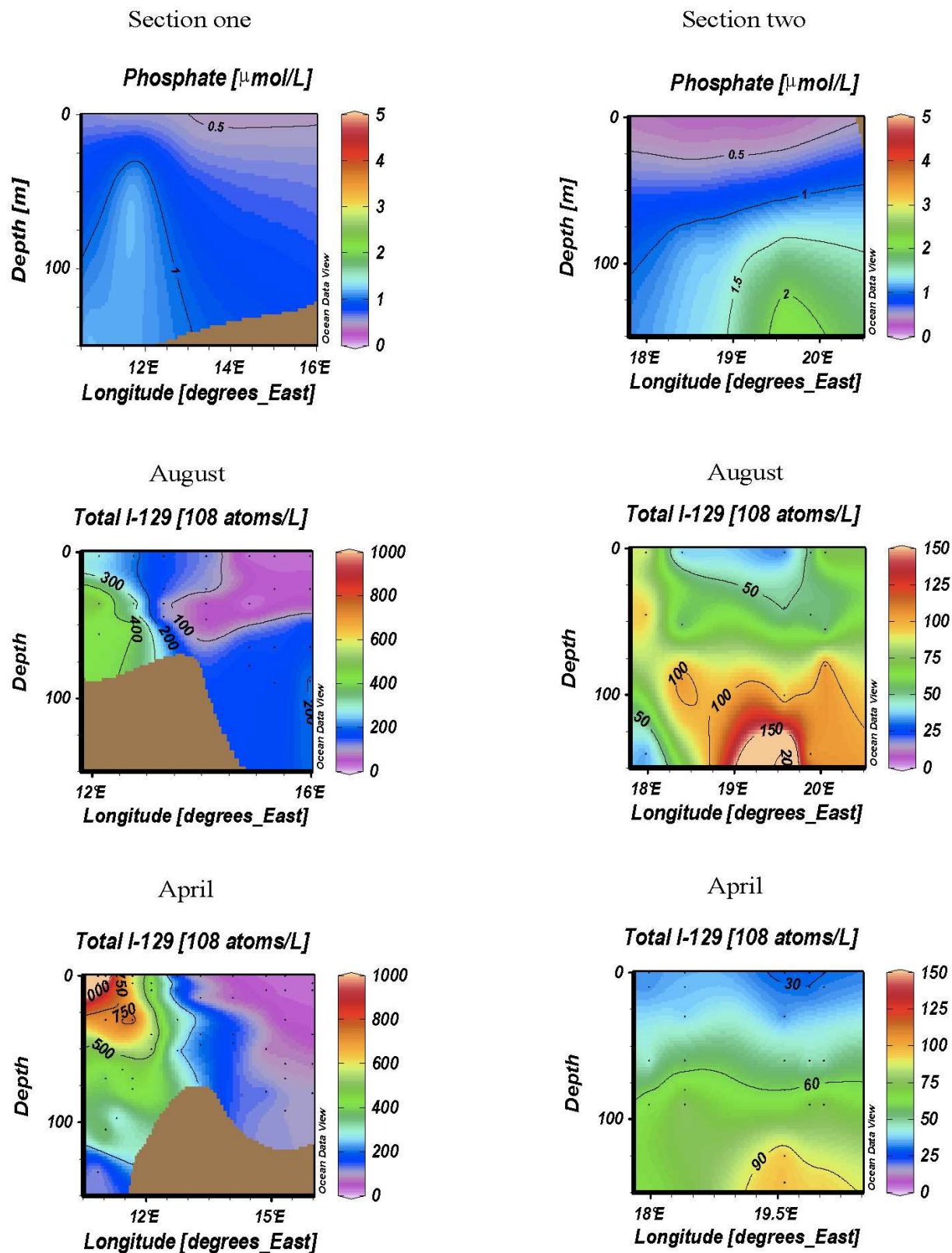


Fig. S-6 A comparison between phosphate and I-129 from August 2006 and April 2007 in section one (Skagerrak and Kattegat basins) and section two (Baltic Proper).

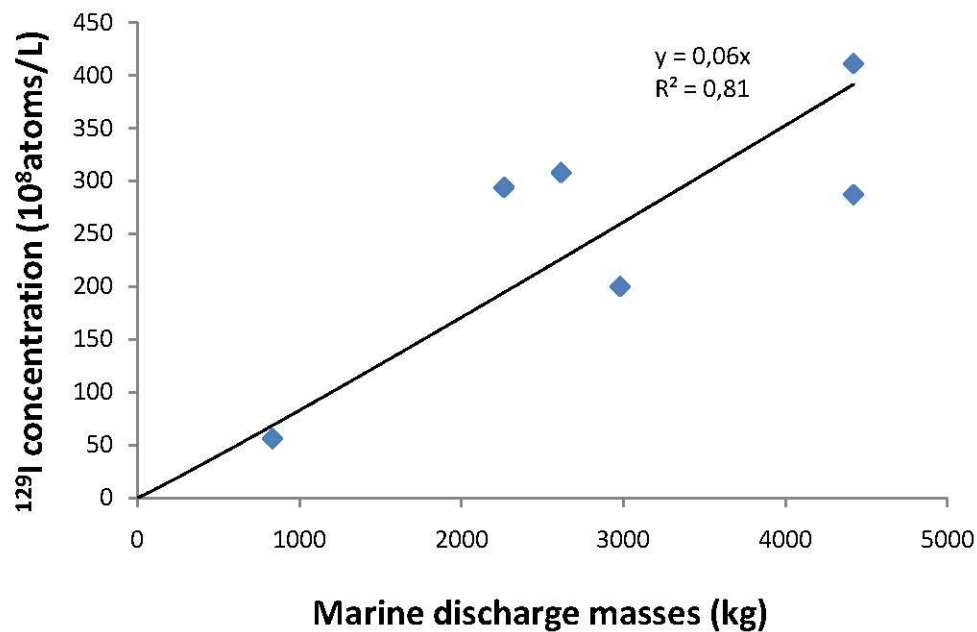


Fig.S-7 Relationship between I-129 concentration and marine discharge masses from Sellafield and La Hague using empirical data near site 14 in the Kattegat. A linear relationship, $y=0.06X$, is applied with $R^2=0.81$.

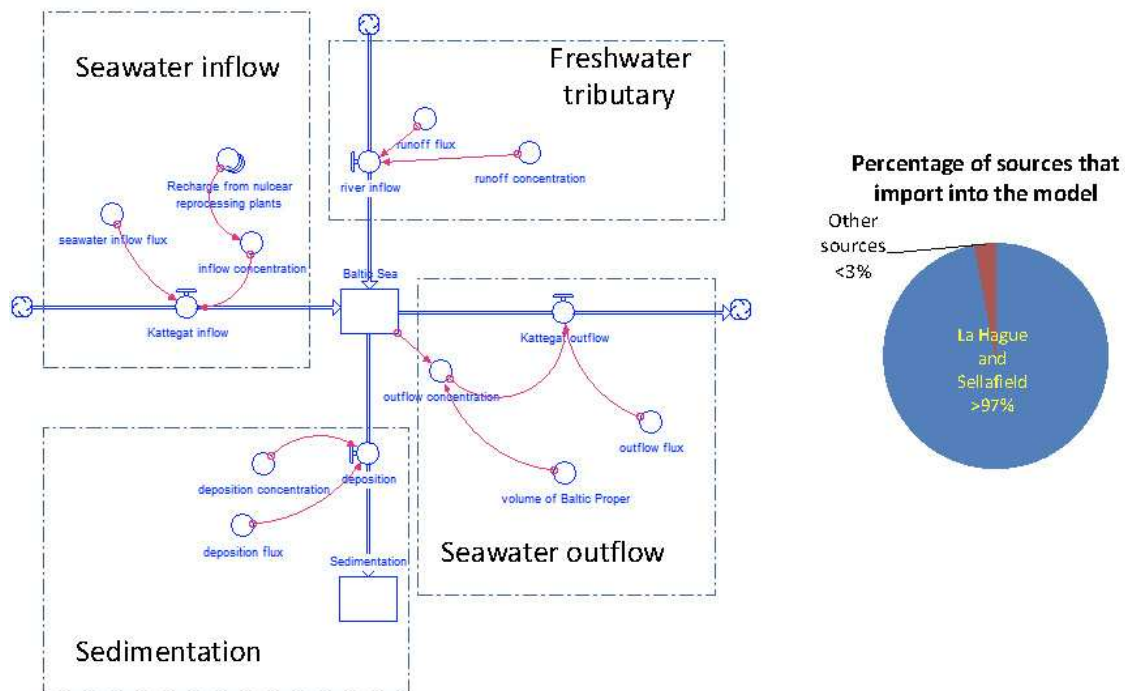


Fig. S-8 General outline of inventory model structure (left) including four compartments (freshwater tributary, sedimentation, seawater inflow and outflow). I-129 input (right) is mainly contributed by marine discharges from the two nuclear reprocessing facilities (La Hague and Sellafield), whereas other sources such as tributary from nuclear weapon tests and the Chernobyl accident total less than 3%.

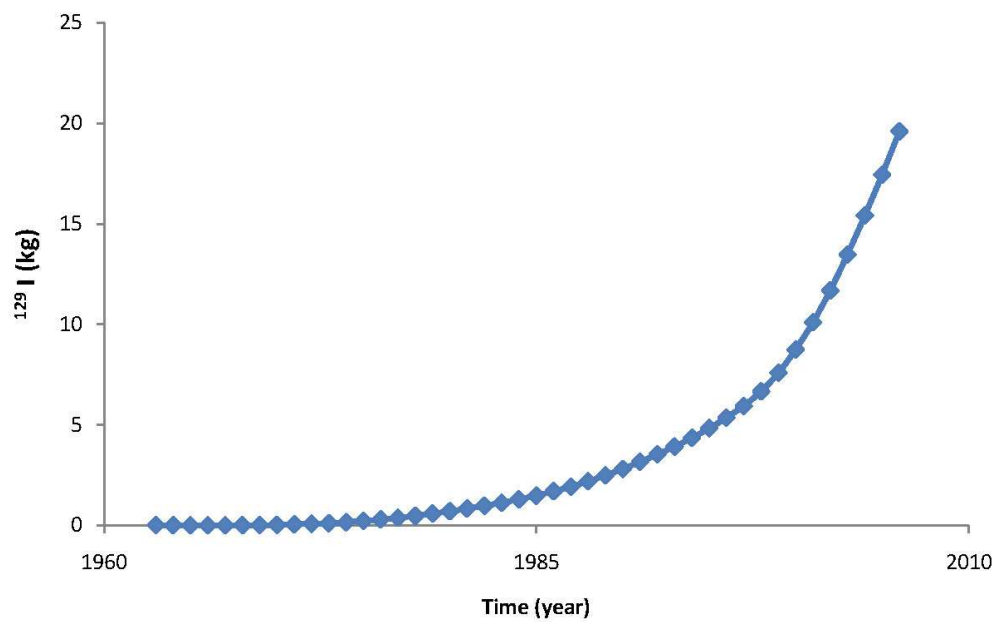


Fig. S-9 Simulated I-129 inventory in the Baltic Proper throughout the years from 1968 to 2006.

Table S-1 Results of I-129 and I-127 in the Baltic Proper, Kattegat and Skaeerrak during August 2006.

Sites number	Latitude	Longitude	Depth m	Temperature °C	Oxygen ml/L	Salinity	¹²⁷ I ppb	¹²⁹ I × 10 ⁸ atoms/L	¹²⁹ I/ ¹²⁷ I × 10 ⁻⁸ atoms/atoms
1	54°59.9' N	13°17.51' E	2,45	18,2	6,04	7,4	15,76	136,19	18,22
			25,09	5,5	6,84	7,5	24,12	149,86	13,10
			35,08	7,7	5,10	8,7	20,93	26,73	2,69
			44,05	10,0	1,43	19,7	32,03	34,30	2,26
2	54°58.44' N	14°5.75' E	2,45	18,7	5,97	7,7	12,38	129,23	22,00
			25,09	15,2	5,68	8,4	17,13	131,15	16,14
			35,08	9,2	5,32	9,2	19,85	26,39	2,80
			45,89	11,4	2,10	19,0	25,08	34,26	2,88
3	55°22.68' N	15°19.77' E	2,45	19,2	6,09	7,3	14,94	31,57	4,45
			25,09	4,3	7,53	7,3	17,65	39,52	4,72
			65,06	6,6	3,97	14,5	24,21	150,84	13,13
			89,33	8,4	1,62	17,2	21,35	168,58	16,64
4	55°15.18' N	15°58.95' E	2,45	19,2	6,03	7,3	15,35	32,11	4,41
			25,09	4,3	7,39	7,4	16,57	42,80	5,44
			65,06	8,2	3,98	14,7	28,51	172,59	12,76
			87,90	7,9	0,85	16,7	36,19	207,34	12,08
5	56°37.72' N	19°35.16' E	2,45	19,7	6,10	6,4	15,31	26,90	3,70
			40,18	3,4	7,57	7,3	18,67	45,30	5,12
			100,14	5,5	1,05	11,4	27,00	73,06	5,71
			142,76	6,1	0,03	12,4	32,07	254,09	16,70
6	57°18.49' N	20°4.74' E	2,45	19,7	5,85	6,5	11,54	88,78	16,22
			55,07	2,2	8,05	7,5	16,03	26,60	3,50
			80,15	5,2	0,73	10,0	17,77	137,59	16,32
			150,31	6,3	0,02	12,2	17,46	39,46	4,76
7	57°59.98' N	19°52.72' E	240,45	6,0	0,01	12,6	21,89	79,09	7,62
			2,45	19,8	5,84	6,5	17,61	41,96	5,02
			45,07	2,4	7,91	7,2	11,66	48,58	8,78
			140,31	6,3	0,03	12,0	22,90	83,40	7,68
8	58°0.9' N	17°58.82' E	195,17	6,2	0,02	12,2	19,89	202,08	21,41
			2,45	19,9	5,92	6,5	10,24	93,77	19,31
			45,07	2,6	7,48	7,2	12,87	100,98	16,54
			140,31	5,4	0,02	10,5	21,72	29,96	2,91
9	57°7.12' N	17°39.94' E	194,97	5,5	0,02	10,6	27,57	35,89	2,74
			2,45	20,2	5,83	7,1	10,14	94,84	19,72
			45,07	4,3	6,87	7,4	16,10	30,47	3,99
			60,16	3,1	6,52	8,1	17,06	42,51	5,25
10	55°33.24' N	18°23.8' E	69,95	4,4	0,87	9,3	25,64	49,24	4,05
			110,13	5,3	0,03	10,3	25,42	70,86	5,88
			2,45	19,6	5,82	7,1	10,54	30,39	6,08
			52,01	2,2	8,01	7,5	10,80	39,33	7,68
11	55°37.11' N	14°51.77' E	89,12	5,4	1,50	11,8	23,36	119,30	10,77
			2,45	18,7	6,01	7,3	7,46	25,58	7,23
			35,08	3,6	7,10	7,6	6,36	16,88	5,59
			65,06	7,5	2,44	15,3	20,90	155,08	15,64
12	55°51.6' N	12°45.01' E	77,50	7,8	0,37	16,4	24,13	166,10	14,51
			2,45	18,1	5,63	17,7	21,51	216,51	21,22
			35,08	7,9	3,44	33,3	35,09	401,33	24,11
			49,97	7,8	3,35	33,3	46,28	519,86	23,68
13	57°11.35' N	11°39.7' E	2,45	18,4	5,49	23,9	28,57	520,94	38,44
			35,08	15,9	4,09	33,5	43,77	892,07	42,97
			55,07	12,4	4,53	33,9	45,79	521,57	24,01
			75,46	9,0	3,98	34,3	52,03	461,60	18,70
14	56°40.45' N	12°6.58' E	2,45	18,5	5,60	19,2	21,79	286,76	27,74
			35,08	11,4	4,18	33,3	34,10	522,94	32,32
			55,88	6,5	2,89	34,0	47,29	419,72	18,71
			77,50	7,8	0,37	16,4	24,13	166,10	14,51
15	57°52.01' N	11°17.86' E	2,45	18,6	5,28	31,6	46,84	942,70	42,42
			25,09	18,5	4,54	32,9	43,16	1883,33	91,98
			45,07	16,6	2,93	33,4	41,57	1692,74	85,84
			90,35	10,8	4,34	34,2	44,00	—	—
16	58°15.59' N	11°26.21 E	2,45	18,6	5,62	25,1	39,80	—	—

Table S-2 Results of I-129 and I-127 in the Baltic Proper, Kattegat and Skaeerrak during April 2007.

Sites number	Latitude	Longitude	Depth m	Temperature °C	Oxygen ml/L	Salinity	¹²⁷ I ppb	¹²⁹ I × 10 ⁸ atoms/L	¹²⁹ I/ ¹²⁷ I × 10 ⁻⁸ atoms/atoms
1	55°00' N	13°18.0' E	0	6,5	9,0	7,8	10,29	36,17	7,41
			15	5,8	8,7	8,1	10,79	38,48	7,52
			40	4,8	6,2	17,4	11,86	195,95	34,83
			47	5,2	5,3	18,4	11,26	173,81	32,54
2	55°00.0' N	14°5.0' E	0	6,9	8,7	7,8	17,48	31,56	3,81
			15	4,7	8,2	8,2	16,88	41,53	5,19
			40	5,5	6,7	12,4	17,54	139,72	16,79
			46	4,7	6,8	16,0	18,11	142,91	16,63
3	55°23.0' N	15°20.0' E	0	6,6	9,4	7,3	7,05	30,99	9,27
			10	4,7	8,7	7,5	8,15	30,59	7,91
			30	4,3	8,2	8,0	7,88	33,60	8,99
			60	4,6	6,6	12,5	8,64	81,52	19,90
			70	6,5	3,5	15,0	8,71	92,74	22,44
4	55°15.0' N	15°59.0' E	92	8,6	0,5	16,2	12,35	105,82	18,06
			5	6,6	9,2	7,6	9,65	36,49	7,97
			10	6,2	9,3	7,7	8,69	29,17	7,08
			40	4,5	8,4	8,0	11,03	39,20	7,49
			60	8,0	2,7	14,0	8,81	77,12	18,45
5	56°38.0' N	19°35.0' E	80	8,7	0,7	16,3	18,03	107,50	12,57
			0	5,3	8,9	7,2	9,21	28,02	6,41
			30	4,0	8,4	7,4	8,68	23,80	5,78
			60	4,1	7,7	7,6	11,40	45,64	8,44
			125	6,5	0,5	12,3	13,49	108,46	16,95
6	57°20.0' N	20°03.0' E	143	6,2	0,1	12,5	11,35	97,68	18,15
			0	4,8	9,2	7,2	12,24	29,95	5,16
			10	4,6	9,3	7,2	12,38	34,30	5,84
			60	3,9	8,3	7,4	12,32	36,60	6,26
			90	5,7	4,0	11,2	14,49	90,54	13,17
7	58°00.0' N	19°53.0' E	150	6,1	0,1	12,3	13,36	96,19	15,18
			225	6,7	0,0	12,6	14,47	108,42	15,79
			0	4,8	9,5	6,9	7,49	25,34	7,13
			10	5,2	9,5	7,1	8,53	27,27	6,74
			60	3,7	8,1	7,3	7,50	29,29	8,23
8	58°01.0' N	17°59.0' E	90	5,3	0,3	10,3	9,82	83,83	18,00
			150	6,0	0,1	12,0	10,73	92,53	18,18
			195	6,0	0,1	12,2	14,90	132,37	18,73
			0	4,2	9,2	6,8	8,66	31,49	7,66
			10	4,1	9,3	6,7	9,49	31,56	7,01
9	57°7.0' N	17°40.0' E	60	3,0	8,0	7,1	22,76	27,81	2,58
			90	5,2	0,3	9,8	25,12	75,26	6,32
			150	5,4	0,1	10,3	15,10	65,53	9,15
			195	5,4	0,1	10,4	24,10	93,39	8,17
			0	4,3	9,2	6,8	8,85	27,82	6,63
10	55°33.3' N	18°24.0' E	10	4,2	9,1	6,8	8,39	27,57	6,93
			50	3,9	8,5	7,2	9,13	34,57	7,98
			80	5,0	0,2	9,7	9,20	13,82	3,16
			100	5,1	0,1	10,1	13,13	83,81	13,46
			109	5,2	0,1	10,2	15,30	11,28	1,55
10	55°33.3' N	18°24.0' E	0	6,4	9,2	7,5	7,44	34,98	9,92

			10	6,3	9,5	7,5	10,43	37,28	7,54
			30	4,5	8,4	7,6	9,84	30,16	6,46
			60	5,8	8,1	7,8	10,27	46,22	9,49
			80	5,3	0,7	10,5	11,60	72,55	13,18
			90	5,8	0,5	11,1	18,45	96,95	11,08
11	55°37.0' N	14°52.0' E	0	6,1	8,8	7,7	8,06	30,21	7,90
			10	6,1	8,8	7,8	10,94	38,04	7,33
			50	4,3	7,8	8,6	11,04	51,53	9,84
			79	8,6	0,7	15,4	19,32	150,69	16,44
12	55°52.0' N	12°45.0' E	0	8,2	7,9	8,7	14,53	81,54	11,83
			10	8,0	7,6	8,8	29,71	66,06	4,69
			30	6,3	3,6	32,0	16,16	294,43	38,41
			51	6,6	3,7	32,8	21,13	137,71	13,74
13	57°11.5' N	11°40.07' E	0	8,5	5,5	23,9	24,41	502,23	43,37
			5	8,1	5,2	24,6	17,23	513,40	62,81
			30	6,3	4,1	33,5	36,36	912,89	52,92
			70	6,9	4,5	33,9	41,15	482,04	24,69
			77	6,9	4,0	34,3	44,63	421,18	19,89
14	56°40.0' N	12°07.0' E	5	8,5	7,3	18,0	20,96	411,12	41,35
			10	8,0	7,2	20,3	23,94	466,00	41,03
			40	6,7	5,2	34,0	39,92	659,61	34,83
			50	6,8	4,8	34,1	48,61	647,87	28,09
15	57°52.0' N	11°18.0' E	0	9,0	7,8	24,0	22,31	655,71	61,96
			10	6,6	7,4	28,5	26,93	739,83	57,91
			30	6,8	6,8	31,8	23,63	632,99	56,47
			97	7,0	5,9	35,1	34,40	229,99	14,09
16	58°15.5' N	11°26. E	0	19,8	7,7	21,1	43,65	718,39	34,69
			10	13,6	7,3	24,3	44,35	852,33	40,51
			30	12,4	5,7	32,3	46,35	837,67	38,10
			64	13,6	4,8	33,2	49,19	418,43	17,93
17	58°20.2' N	11°02 E	0	9,0	7,4	30,0	33,52	1682,92	105,83
			5	8,9	7,6	30,2	27,06	912,47	71,08
			30	6,9	6,7	32,4	41,71	728,28	36,81
			70	6,9	5,9	33,3	39,84	372,30	19,70
			105	6,8	5,8	33,4	43,81	412,40	19,84
18	58°17.7' N	10°51 E	0	9,3	7,5	27,5	32,13	1296,56	85,06
			5	15,1	7,3	29,0	38,35	1169,82	64,30
			50	13,8	6,3	34,2	42,81	453,15	22,31
			134	14,2	5,9	35,1	37,45	109,81	6,18
19	58°16.5' N	10°30.8 E	0	8,1	7,4	27,0	32,04	1394,85	91,77
			5	8,0	7,5	27,0	32,28	1728,43	112,87
			10	6,5	7,3	28,2	41,96	1514,85	76,10
			40	6,8	6,3	34,1	37,07	843,52	47,97
			75	7,5	5,8	35,1	36,67	436,14	25,07
			200	7,0	6,2	35,3	46,07	106,10	4,85
			300	7,0	6,1	35,5	52,54	72,35	2,90

Table S-3 I-129 data in surface waters of the Baltic Proper, Kattegat and Skagerrak from published references

Sites	Year	^{129}I Concentration ($\times 10^8$ atoms/L)	References
Baltic Proper	1992	11	12
	1999	75	3
	1999	11	13
	1999	12	13
	1999	42	13
	2001	11	8
	2001	10	8
	2001	13	8
	2001	14	8
	2001	14	8
	2001	25	8
	2001	21	8
	2001	24	8
	1992	56	12
	1999	313	13
Kattegat	1999	319	13
	1999	558	13
	2000	518	3
	2000	313	3
	2001	499	8
	2001	200	8
	1999	530	13
	2000	2400	3
Skagerrak	2000	2680	3
	2000	1938	3

Table S-4 Inventory estimation of I-129 in the Baltic Proper, Kattegat and Skagerrak (August 2006-April 2007).

Basin	Layer	Volume (km ³)	^{129}I concentration in August ($\times 10^8$ atoms/L)	^{129}I concentration in April ($\times 10^8$ atoms/L)	^{129}I inventory in August (kg)	^{129}I inventory in April (kg)
Kattegat	surface	220	540±324	556±475	2.5±1.5	2.6±2.2
	deep	295	467±51	389±252	3.0±0.3	2.5±1.6
Baltic Proper	surface	7409	52±26	33±10	8.2±4.1	5.2±1.6
	middle	3144	110±71	54±27	7.4±4.8	3.6±1.8
	deep	2784	144±109	93±82	8.6±6.5	5.5±4.9
Skagerrak	surface	142	—	1420±251	—	4.3±0.1
	middle	426	—	577±141	—	5.3±0.2
	deep	852	—	96±24	—	1.8±0.1

Paper III

Hansen, V., Yi, P., Hou, X., Roos, P., Aldahan, A., Possnert, G. Iodide and iodate (^{129}I and ^{127}I) in surface water of the Baltic Sea, Kattegat and Skagerrak. *Science of the Total Environment* 412-413 (2011) 296–303



Iodide and iodate (^{129}I and ^{127}I) in surface water of the Baltic Sea, Kattegat and Skagerrak

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ARTICLE INFO

Article history:

Received 16 June 2011

Received in revised form 30 September 2011

Accepted 3 October 2011

Available online 26 October 2011

Keywords:

^{129}I

^{127}I

Baltic Sea speciation

AMS

ICP-MS

ABSTRACT

Despite the common incorporation of iodine in the biological cycle and occurrence of huge contamination of the radioactive isotope ^{129}I in the Baltic Proper, Skagerrak and Kattegat, there is no data on chemical speciation of iodine in these waters. We here present first time data on iodine isotopes ^{129}I and ^{127}I species as iodide and iodate in surface seawater samples collected from 16 locations in August 2006 and 19 locations in April 2007 in the Baltic Proper, Skagerrak and Kattegat. After extensive separation methods, the isotopes concentrations were determined using accelerator mass spectrometry (AMS) technique for the ^{129}I and inductively coupled plasma mass spectroscopy (ICP-MS) for ^{127}I . High concentrations of both isotopes species were found in the Skagerrak–Kattegat basins, whereas the values in the Baltic Proper are low for both species. The ratios of $^{129}\text{I}^-/^{129}\text{IO}_3^-$ and $^{127}\text{I}^-/^{127}\text{IO}_3^-$ significantly increase from south to central Baltic Sea, and iodide (both isotopes) appears as the predominant inorganic iodine species along the Baltic Sea. The results show insignificant change in ^{129}I and ^{127}I speciation and suggest that reduction of iodate and oxidation of iodide in Skagerrak and Kattegat may be a slow process. Additionally, the positive correlation between salinity and iodide and iodate (both isotopes) may reflect effective control of Skagerrak water mass on iodine distribution in surface water of the Baltic Sea.

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1. Introduction

Iodine is a redox sensitive element with oxidation states -1 , 0 , $+1$, $+3$, $+5$ and $+7$. Although in seawater iodine exists mainly as iodide, iodate and to a lesser extent as organic iodine occur (Wong, 1991; Wong and Zhang, 2003; Hou et al., 2009). In oxic marine waters iodate is the thermodynamically stable form while in anoxic seawater, such as the deep waters of the Black Sea and the Baltic Sea, iodide should constitute the major species of iodine (Wong, 1991; Tian and Nicolas, 1995; Truesdale et al., 2001; Hou et al., 2001; Wong and Zhang, 2003; Hou et al., 2009). Despite this, it is still unclear how iodide can exist in highly oxygenated surface waters or how iodate occurs in anoxic water. Attempts to explain the reduction of iodate to iodide in seawater have demonstrated (Tsunogai and Sase, 1969) that certain organisms enzymatically (nitrate-reductase) are able to reduce iodate to iodide. The reduction of iodate to iodide has been shown in batch culture of different marine phytoplankton species at both ambient and elevated iodate levels ($5\text{--}10\text{ }\mu\text{M}$) (Wong et al., 2002; Chance et al., 2007; Bluhm et al., 2010). Campos et al. (1999)

indicated that there might be a linkage between the iodide production and nitrate concentration, showing that the iodide levels were increased as nitrate concentrations decreased. Through observations of the iodate–iodide redox behavior in North Sea surface water, Spokes and Liss (1996) showed that iodide is photochemically produced through iodate reduction and the organic matter plays an important role in this process. Isotopic tracer studies conducted in laboratories (Amachi et al., 2004) with the aim of understanding the converting mechanism of iodine species have been less conclusive, probably because laboratory experiments usually have difficulties in mimicking all the complex processes occurring in real marine environments. Several studies up to date on ^{127}I chemical speciation (as iodide and iodate) have been carried out in order to investigate the marine biogeochemical cycle of iodine (Wong and Zhang, 2003; Truesdale and Upstill-Goddard, 2003; Waite et al., 2006) and to obtain insight into the mechanisms of iodate reduction/iodide oxidation in seawater (Tian and Nicolas, 1995; Truesdale et al., 2001; Hou et al., 2007). Despite all studies, there is still a lack in understanding the marine biogeochemical cycle of iodine, reduction/oxidation mechanism of iodine species and how fast the process proceeds in marine environment.

Recently, chemical speciation analysis of ^{129}I has been applied for studying the geochemistry of stable iodine in marine environment,

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conversion process between iodide and iodate, distribution and transport pathways of iodine species in marine water as well as tracing terrestrial organic carbon (Hou et al., 2001; Schwehr et al., 2005; Hou et al., 2007).

Naturally occurring ^{127}I distributes widely in the atmosphere, lithosphere, hydrosphere and biosphere at different concentrations. Natural ^{129}I is produced by cosmic-ray-induced spallation of xenon in the upper atmosphere, spontaneous fission of ^{238}U in the geosphere and in minor quantities, by neutron bombardment of tellurium. Thermal neutron induced fission of ^{235}U is another minor natural source in the lithosphere. The estimated atomic ratio of $^{129}\text{I}/^{127}\text{I}$ in the pre-nuclear era is about 10^{-12} to 10^{-13} in the marine environment (Hou et al., 2009). Before the human nuclear activities ^{129}I concentration in the Baltic Sea was estimated to be 10^{-17} g/l (Hou et al., 2002). In recent years the input of anthropogenic ^{129}I has completely overriden the natural environmental concentration by several orders of magnitude (Hou et al., 2002; Alfimov et al., 2004; Aldahan et al., 2007; Hou et al., 2009). In the Baltic Sea the ^{129}I sources include, apart from natural occurrence, fallout from atmospheric nuclear weapon tests, the Chernobyl accident, releases from nuclear power plants and discharges from nuclear fuel reprocessing plants. Contributions of ^{129}I from nuclear weapon tests, Chernobyl accident and nuclear power stations to the Baltic Sea are comparatively insignificant (Hou et al., 2002; Aldahan et al., 2006), leaving mainly the discharge from reprocessing as the significant source. During 1999–2009, respectively 14.6 and 4.6 TBq of ^{129}I have been discharged in to the English Channel from the La Hague reprocessing plant and to the Irish Sea from the Sellafield reprocessing plant (www.ospar.org). Dahlgard et al. (1995) estimated that roughly 10% of the La Hague (English Channel) and 2% of the Sellafield (Irish Sea) releases are transported into Kattegat and further into the Baltic Sea.

The relatively long half life of ^{129}I (15.7 myr) and long residence time (30 kyr) in the marine environment as well as continuous releases from nuclear fuel reprocessing facilities make this isotope a suitable transient tracer for the study of marine biogeochemical cycle of stable iodine through its chemical speciation.

The aim of the present study was to reach further into understanding of the iodate reduction/iodide oxidation behavior by studying these species in surface seawater ranging from full salinity Skagerrak water to brackish water in the Baltic Sea Proper, at the same time covering two different seasons. The influences of some relevant seawater parameters such as oxygen, and salinity on changes in iodine speciation in seawater were also investigated. In particular, we wanted to approach the question whether stable iodine and ^{129}I at the moment behave in the same way in long term reservoirs like marine systems, despite the recent addition of ^{129}I in the environment. The colossal anthropogenic discharges of ^{129}I as liquid and gases from reprocessing plants raise some questions about the isotopic equilibrium and chemical speciation of ^{129}I and ^{127}I in long term reservoirs like marine systems.

The radiological importance of ^{129}I is so far of minor importance due to the very low activity concentrations encountered even close to reprocessing plants but this radioisotope is well suited as a tracer to better understand the behavior of iodine in the environment. Furthermore iodine-129 can also be released in reactor accidents (e.g. Chernobyl and Fukushima accidents) due to its high volatility, and can in this context serve as a retrospective tracer shedding new light on the environmental behavior of the radiologically much more important, but also much more short-lived ^{131}I .

So far there are relatively few data on the chemical speciation of ^{129}I in seawater (Hou et al., 2001, 2007) and a few studies carried out with a focus on seasonal changes (Truesdale et al., 2003; Chance et al., 2010). Therefore, addition of new seawater data sets will certainly expand our understanding of the iodine cycle in general and the radioactive isotope in particular. We here report on the

occurrence of iodine isotopes and their speciation in surface water collected in the Baltic Sea, Kattegat and Skagerrak Basin.

2. Sampling and analytical methods

2.1. Hydrographic area studied

The area studied (Fig. 1) includes Skagerrak, Kattegat and Baltic Sea. The Skagerrak represents a mixture of three water masses, namely surface North Sea water, deep Atlantic water and surface water from the Kattegat (Rydberg et al., 1996). The Kattegat represents a mixture of surface and deep water of Skagerrak and outflow of the Baltic Sea surface water (Yi et al., 2011). The Baltic Sea is a marginal shallow landlocked sea. Water exchange with the open ocean through the North Sea occurs only through the shallow and narrow Danish Straits. Open ocean water inflow through these straits combined with a large fresh water inflow in the Baltic proper creates a salinity gradient along the entire Baltic Sea from around 25‰ in the transition areas down to 3‰ in the Gulf of Bothnia (Truesdale et al., 2001; Grasshoff, 1975; Bendtsen et al., 2009). In this respect the Baltic Sea can be regarded as a large estuary. Because of the strong influence of rivers water, the composition of this low salinity water differs from ocean water (Grasshoff, 1975). Other representatives of this category are the Black Sea and a considerable number of fjords. Due to the restricted inflow of oxygenated saline water and the presence of several deep basins isolated by shallow and narrow sills several of these basins have oxygen deficient bottom waters. Such oxygen deficient and anoxic waters have been characteristic of the Baltic Sea throughout its entire history as a brackish sea (Bendtsen et al., 2009; Grasshoff, 1975; Conley et al., 2002). The strong water stratification coupled with a long average residence time (25–35 years) of Baltic Sea water and the shallow average depth of around 60 m make the sediment an important compartment for biogeochemical cycles for both nutrients and pollutants. The oscillations in near bottom water oxygen and the redox mediated cycling of several sediment constituents make the sediments an important reservoir for fluxes back to the water column. The large inflow of fresh water from surrounding boreal forest areas furthermore enriches the Baltic Sea with dissolved organic matter and nutrients (Grasshoff, 1975). Taken altogether the Baltic Sea is a fairly complicated system with both strong variations in salinity, oxygen and DOC. Apart from these factors seasonal variations add to its complexity.

In the studied surface waters salinity varied between 18‰ and 32‰ in the Skagerrak and Kattegat, whereas it was found to be 17‰ in the Belt Sea in August 2006 (but only slightly more than 8‰ in April 2007) and less than 8‰ through Baltic Sea (Fig. 5).

Along the Skagerrak, Kattegat and Belt Sea oxygen vary within 5.3–8 ml/L for both seasons (Fig. 5). Through Baltic Sea surface water oxygen values vary within 5.8–9.5 ml/L for both seasons (Fig. 5).

2.2. Samples and reagents

Sampling was carried out on board the research Vessel Argos, operated by the marine division of the Swedish Meteorological and Hydrological Institute. Surface (0–15 m) samples were collected in Nansen bottles (Hydro Bios) from 19 locations in the Baltic Sea, Kattegat and Skagerrak Basin in August 2006 and 16 identical stations in April 2007 (Fig. 1). A CTD-model SD204 was used to measure the salinity which was also measured on board, using an AEG MINISAL 2100 salinometer based on relative conductivity. Oxygen was determined by the Winkler titration method.

The samples (for ^{129}I and ^{127}I analysis) were filtered through a 0.45 µm pore size (Sartorius AG, Gottingen, Germany), closed tight and stored in clean polyethylene containers until analysis. All chemical reagents used were of analytical grade, and all solutions were prepared using deionized water ($>18.2\ \Omega$). A diluted ^{129}I standard

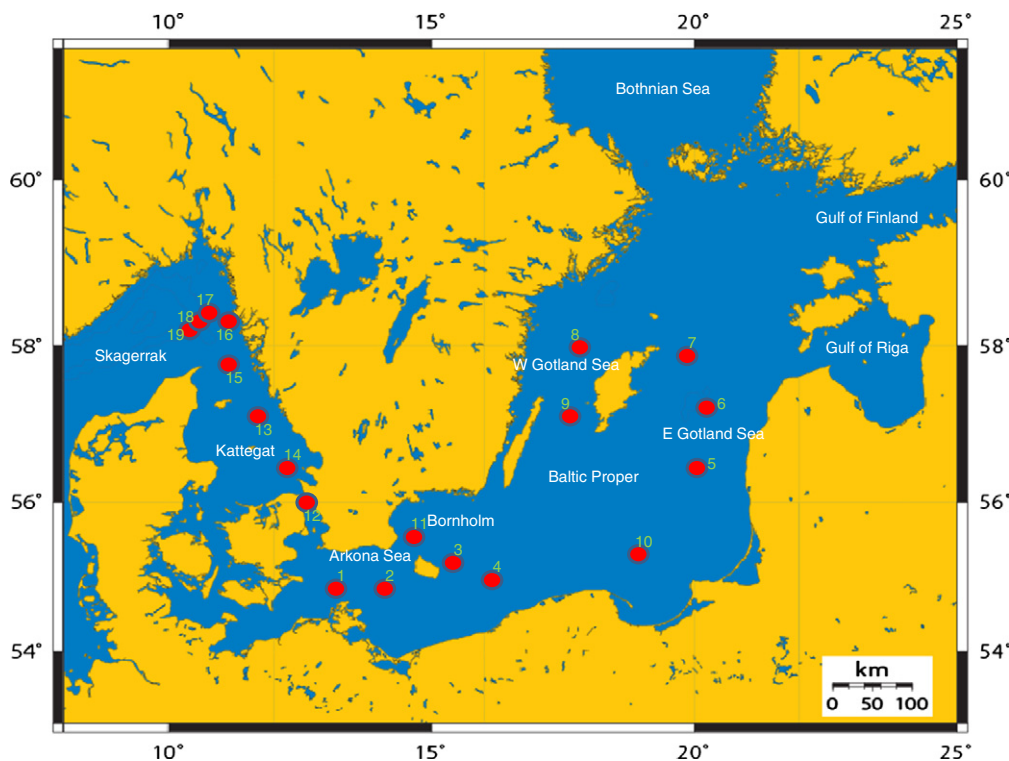


Fig. 1. Sampling stations of surface water in the Skagerrak, Kattegat and Baltic Sea for August 2006 (stations 1–16) and April 2007 (stations 1–19).

(prepared from NISTSRM 4949C) with a $^{129}\text{I}/^{127}\text{I}$ ratio of 1.1×10^{-11} , ^{125}I tracer (Amersham Pharmacia Biotech, Little Chalfont, Buckinghamshire, UK), ^{127}I carrier (Woodward iodine, MICAL Specialty Chemicals, New Jersey) and Bio-Rad AG1-x4 anion exchange resin (Bio-Rad laboratories, Richmond, CA) were used.

2.3. Separation of iodine species as iodide and iodate

A modified version of the analytical method of Hou et al. (2007) was used for the separation of iodide and iodate. Bio-Rad AG1-x4 strongly basic anion exchange resin, 50–100 mesh was converted to NO_3^- form and packed in a column of $\varnothing 1.0 \times 20$ cm. Around 100–300 mL of seawater spiked with about 50 Bq of $^{125}\text{I}^-$ tracer was loaded onto the column at a flow rate of 1 mL min^{-1} . The column was then washed with 30 mL of distilled water and 50 mL of 0.2 M KNO_3 . The effluent and the fluid from washing process were combined for the determination of iodate. Iodide on the column was eluted using 40 mL of 10% NaClO .

About 50 Bq of a $^{125}\text{I}^-$ solution was added to effluent–wash mixture (iodate fraction) as chemical yield tracer. About 2.0 mg of stable iodine (prepared from Woodward iodine) was added to iodide and effluent–wash mixture (iodate fraction) as a carrier. To convert all iodine to iodide, 0.2 mL of 2.0 M NaHSO_3 was added to effluent–wash mixture and the pH was adjusted to 2 using 3.0 M HNO_3 . Iodine was first extracted with CCl_4 after oxidation of iodide to molecular iodine using NaNO_2 , and then back-extracted with NaHSO_3 solution. The extraction and back-extraction was repeated to recover all iodine in the solution. The chemical yields of iodide and iodate were measured by counting ^{125}I in the separated solution using a NaI γ -detector, and were found to be 50–71% and 63–91% respectively.

Iodine in the separated solution (as iodide) was afterwards precipitated as AgI by addition AgNO_3 .

2.4. ^{127}I and ^{129}I preparation for ICP–MS and AMS measurement

One milliliter of eluate (for iodide) was taken and diluted to 20 mL with 0.1 M NH_4OH . Approximately 10 mL of the effluent–wash

mixture (iodate fraction) was spiked with a NH_4OH solution to reach a final concentration of 0.1 M. Cs^+ as (CsCl) was added as an internal standard to a concentration of 2.0 ng/mL. The concentration of ^{127}I was determined using an X SeriesII ICP–MS (Thermo Electron Corporation). The detection limit, calculated as 3SD of blanks, was 0.28 nM.

AgI was mixed with niobium powder and pressed into a copper holder for measurements of ^{129}I by accelerator mass spectrometry (AMS) at the Tandem Laboratory, Uppsala University using a terminal voltage of 3.5 MV. The statistical error of the analysis including mainly measurement errors at 1 standard deviation was <10%, as blank correction was negligible.

3. Results

3.1. ^{127}I -iodide and ^{127}I -iodate in surface water of Baltic Sea, Kattegat and Skagerrak

The concentrations of ^{127}I (as iodide and iodate) and their ratios for August 2006 and April 2007 sampling campaigns are listed in Tables 1 and 2. The spatial distribution of ^{127}I (as iodide and iodate), ^{127}I -iodide/ ^{127}I -iodate, $^{129}\text{I}/^{127}\text{I}$ iodide (10^{-8}) and $^{129}\text{I}/^{127}\text{I}$ iodate (10^{-8}) in surface water are shown in Figs. 2 and 4. The distribution of ^{127}I -iodide shows, for both sampling campaigns, a rather uniform decrease from the Skagerrak to the central part of the Baltic (Fig. 2a and d). Maximum ^{127}I -iodide reaches about 28.2 ppb in the Skagerrak basin and the minimum is 5.6 ppb in the Bornholm basin. The ^{127}I -iodide seems rather homogenous in the surface water of the respective basins and also the dominant iodine species in samples measured. Unlike the iodide, distribution of ^{127}I -iodate shows some spatial differences between the two sampling campaigns (Fig. 2b and e). On average there is less iodate during April than during August, but the maximum ^{127}I -iodate value (33.4 ppb) is still found in the Skagerrak–Kattegat. The minimum value appears within the southeastern part of the Baltic Sea at value of 0.3 ppb. There appears also to be persistent relatively high values (5–9 ppb) of ^{127}I -iodate occurring along

Table 1

Analytical results of $^{129}\text{I}^-$, $^{127}\text{I}^-$ and $^{129}\text{IO}_3^-$, $^{127}\text{IO}_3^-$, $^{129}\text{I}^-/^{127}\text{I}^-$, $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$, $^{129}\text{I}^-/^{127}\text{I}^-$, $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$ in surface water from Skagerrak, Kattegat and Baltic Sea for samples collected in August 2006.

Station number	Latitude	Longitude	Depth, m	^{127}I iodide, ppb	^{127}I iodate, ppb	^{127}I iodide/ iodate	^{129}I iodide \times 10^8 atoms/L	^{129}I iodate \times 10^8 atoms/L	^{129}I iodide/ iodate	$^{129}\text{I}/^{127}\text{I}$ iodide \times 10^{-8}	$^{129}\text{I}/^{127}\text{I}$ iodate \times 10^{-8}
1	54°59.9'N	13°17.51' E	2.4	12.1	3.6	3.4	130.7	2.7	48.6	22.7	1.6
2	54°58.44'N	14°5.75' E	2.4	8.7	3.7	2.4	129.0	1.3	95.6	31.2	0.8
3	55°22.68'N	15°19.77' E	2.4	11.6	3.4	3.4	28.1	3.2	8.8	5.1	2.0
4	55°15.18'N	15°58.95' E	2.4	11.4	4.0	2.9	22.9	9.3	2.5	4.3	4.9
5	56°37.72'N	19°35.16' E	2.4	11.7	3.6	3.3	25.0	2.6	9.7	4.5	1.5
6	57°18.49'N	20°4.74' E	2.4	6.4	5.1	1.3	84.0	3.5	24.2	27.5	1.4
7	57°59.98'N	19°52.72' E	2.4	8.2	9.4	0.9	38.9	3.7	10.5	10.0	0.8
8	58°0.9'N	17°58.82' E	2.4	7.6	2.6	2.9	90.0	1.8	50.0	24.9	1.4
9	57°7.12'N	17°39.94' E	2.4	7.3	2.8	2.6	87.9	3.0	28.9	25.3	2.3
10	55°33.24'N	18°23.8' E	2.4	8.6	1.9	4.5	29.9	2.6	11.5	7.3	2.9
11	55°37.11'N	14°51.77' E	2.4	5.7	1.8	3.2	23.5	2.3	10.3	8.7	2.7
12	55°51.6'N	12°45.01' E	2.4	8.6	12.9	0.7	143.7	78.8	1.8	35.1	12.9
13	57°11.35'N	11°39.7' E	2.4	9.3	19.3	0.5	393.7	122.4	3.2	89.2	13.4
14	56°40.45'N	12°6.58' E	2.4	8.8	13.0	0.7	195.7	93.3	2.1	47.1	15.1
15	57°52.01'N	11°17.86' E	2.4	13.4	33.4	0.4	567.3	341.9	1.7	89.0	21.6
16	58°15.59'N	11°26.21 E	2.4	19.1	20.7	0.9	267.3	179.6	1.5	29.6	18.3

the northeastern part of the Baltic Sea for both sampling campaigns (Tables 1 and 2).

Differences between the ratio of ^{127}I -iodide/ ^{127}I -iodate (in atoms/atoms) for the two sampling campaigns indicate occurrence of relatively low values in the Skagerrak–Kattegat basin and higher ratios within the

Baltic proper (Fig. 2c and f). The ratios are, however, less during August when compared to the April. Maximum ^{127}I -iodide/ ^{127}I -iodate value occurs within the Baltic Sea proper during April, whereas a specifically high ratio (Fig. 2c and f) area appears in the southeastern part of the Baltic Sea during August and this zone is also found during April.

Table 2

Analytical results of $^{129}\text{I}^-$, $^{127}\text{I}^-$ and $^{129}\text{IO}_3^-$, $^{127}\text{IO}_3^-$, $^{129}\text{I}^-/^{127}\text{I}^-$, $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$, $^{129}\text{I}^-/^{127}\text{I}^-$, $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$ in surface water from Skagerrak, Kattegat and Baltic Sea for samples collected in April 2007.

Station number	Latitude	Longitude	Depth, m	^{127}I iodide, ppb	^{127}I iodate, ppb	^{127}I iodide/ iodate	^{129}I iodide \times 10^8 atoms/L	^{129}I iodate \times 10^8 atoms/L	^{129}I iodide/iodate	$^{129}\text{I}/^{127}\text{I}$ iodide \times 10^{-8}	$^{129}\text{I}/^{127}\text{I}$ iodate \times 10^{-8}
1	55°00'N	13°18.0' E	0	8.8	0.3	32.6	33.1	3.6	9.3	7.9	27.8
			15	9.1	0.3	31.5	35.1	4.5	7.8	8.1	32.8
2	55°00.0'N	14°5.0' E	0	11.2	2.4	4.7	32.1	3.6	8.9	6.0	3.2
			15	11.3	2.4	4.8	39.7	4.6	8.7	7.4	4.1
3	55°23.0'N	15°20.0' E	0	7.8	0.6	13.8	28.4	3.2	9.0	7.6	11.7
			10	5.6	0.7	8.0	27.7	2.4	11.5	10.4	7.2
4	55°15.0'N	15°59.0' E	5	8.7	1.0	9.0	37.1	2.4	15.4	9.0	5.3
			10	5.6	0.6	10.1	26.6	3.7	7.2	10.1	14.1
5	56°38.0'N	19°35.0' E	0	8.7	0.9	9.7	27.6	2.0	13.8	6.7	4.7
			10	9.9	1.2	8.1	29.0	1.8	16.3	6.2	3.1
6	57°20.0'N	20°03.0' E	0	9.0	1.6	5.6	30.8	2.6	11.9	7.2	3.4
			10	10.0	4.1	2.5	24.4	1.3	18.7	5.1	0.7
7	58°00.0'N	19°53.0' E	0	10.5	5.1	2.1	25.6	2.3	11.1	5.1	0.9
			10	8.8	0.5	19.5	27.6	1.5	18.4	6.6	7.0
8	58°01.0'N	17°59.0' E	0	9.6	0.4	27.3	29.8	1.8	16.7	6.6	10.8
			10	7.2	0.4	18.6	25.0	1.7	14.6	7.3	9.2
9	57°7.0'N	17°40.0' E	0	7.2	0.4	16.4	24.0	1.1	21.3	7.0	5.4
			10	7.0	0.5	13.8	33.1	2.7	12.3	10.0	11.3
10	55°33.3'N	18°24.0' E	0	9.3	0.7	13.2	32.8	3.3	10.0	7.5	9.9
			10	15.3	0.9	16.3	21.3	3.2	6.6	2.9	7.3
11	55°37.0'N	14°52.0' E	0	9.2	1.3	7.3	37.3	3.5	10.5	8.6	5.9
			10	10.3	1.0	10.0	62.1	11.3	5.5	12.7	23.1
12	55°52.0'N	12°45.0' E	0	4.6	23.0	0.2	64.9	4.0	16.2	29.5	0.4
			10	15.8	9.0	1.8	353.9	178.7	2.0	47.3	42.0
13	57°11.5'N	11°40.07' E	0	8.1	8.1	1.0	384.6	167.5	2.3	100.3	43.4
			5	14.6	4.4	3.3	267.5	136.7	2.0	38.5	65.1
14	56°40.0'N	12°07.0' E	0	18.7	6.9	2.7	321.2	114.8	2.8	36.3	35.1
			10	12.2	10.3	1.2	323.0	339.6	1.0	56.0	69.2
15	57°52.0'N	11°18.0' E	0	8.2	18.3	0.4	438.6	300.1	1.5	112.2	34.5
			10	14.9	29.0	0.5	472.1	252.7	1.9	66.8	18.4
16	58°15.5'N	11°26. E	0	17.5	28.1	0.6	512.5	346.9	1.5	61.7	26.0
			10	18.0	12.4	1.5	1097.7	500.0	2.2	128.9	85.3
17	58°20.2'N	11°02 E	0	18.1	6.2	2.9	721.4	195.0	3.7	84.1	66.8
			5	28.2	5.2	5.4	760.0	580.8	1.3	56.9	235.3
18	58°17.7'N	10°51 E	0	23.8	14.6	1.6	392.6	723.3	0.5	34.8	104.5
			5	13.9	15.0	0.9	880.6	548.2	1.6	133.6	77.0
19	58°16.5'N	10°30.8 E	0	14.7	17.4	0.8	965.2	777.1	1.2	138.0	94.4
			10	17.9	17.3	1.0	1004.0	545.1	1.8	118.2	66.6

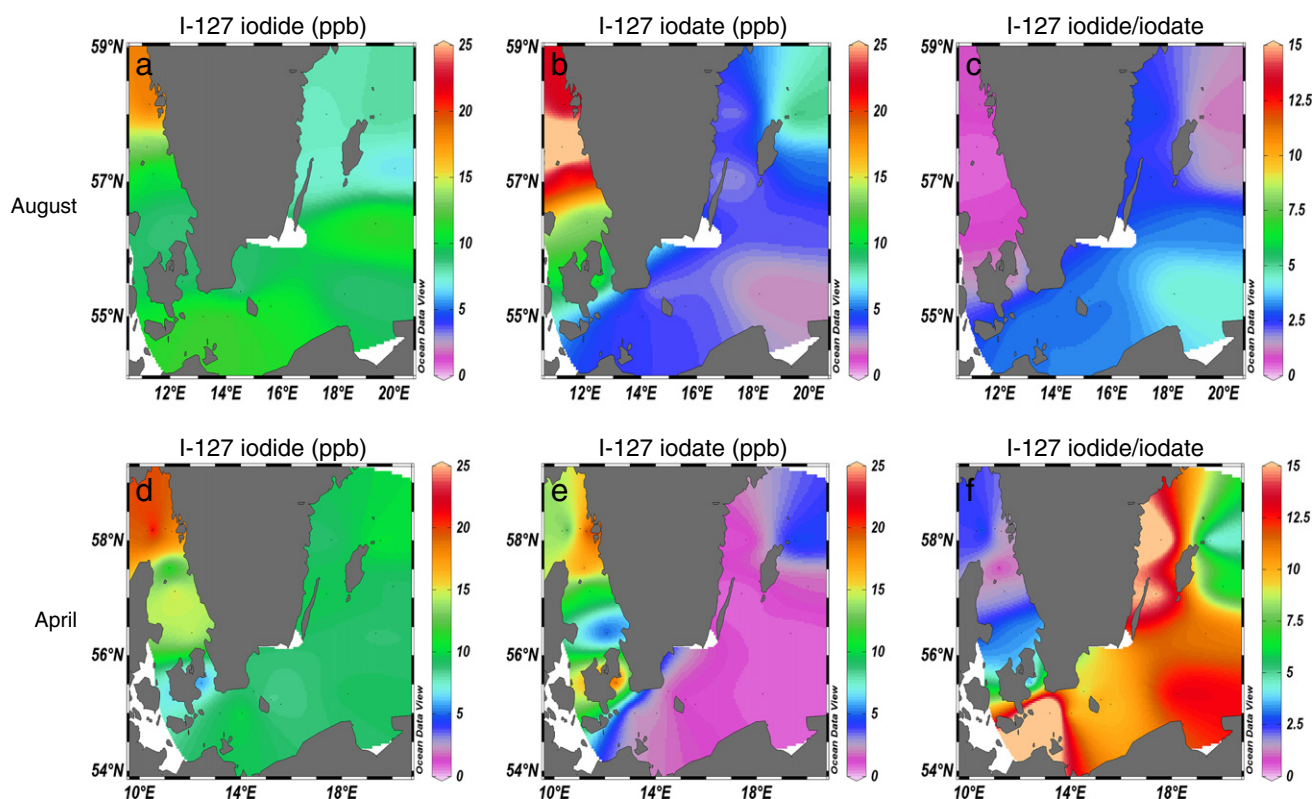


Fig. 2. Distribution of $^{127}\text{I}^-$, $^{127}\text{IO}_3^-$ and $^{127}\text{I}^-/^{127}\text{IO}_3^-$ (a–f) in the surface water of Skagerrak, Kattegat and Baltic Sea for samples collected in August 2006 and April 2007.

3.2. ^{129}I -iodide and ^{129}I -iodate in surface water of Baltic Sea, Kattegat and Skagerrak

The concentrations of ^{129}I (as iodide and iodate) and their ratios for August 2006 and April 2007 sampling campaigns are listed in Tables 1 and 2. The spatial distribution of ^{129}I (as iodide and iodate), ^{129}I -iodide/ ^{129}I -iodate, $^{129}\text{I}/^{127}\text{I}$ iodide (10^{-8}) and $^{129}\text{I}/^{127}\text{I}$ iodate (10^{-8}) in surface water is shown in Figs. 3 and 4.

The distribution of ^{129}I species seems homogenous for both ^{129}I -iodide and ^{129}I -iodate, where the decrease in their concentrations follows the surface water mass from the Skagerrak to the north part of the Baltic proper (Fig. 3a, b, d and e). Similar to the behavior of ^{127}I -iodide, the ^{129}I -iodide is the dominant species compared to iodate. Maximum value of ^{129}I -iodide over 1000×10^8 atoms/L at the Skagerrak basin, whereas the minimum value is around 25×10^8 atoms/L and occurs in the Baltic Proper. For the ^{129}I -iodate, the range for minimum and maximum values is at $1.1\text{--}9.3 \times 10^8$ atoms/L and $4\text{--}777 \times 10^8$ atoms/L in the Skagerrak and Baltic Proper respectively. The ratio between the ^{129}I -iodide/ ^{129}I -iodate is up to five times higher than for the ^{127}I -iodide/ ^{127}I -iodate and the spatial pattern contains more differentiation within the Baltic Sea during August than during April (Fig. 3c and f). Maximum ratio of 95.6 appears in the Arkona Basin and West Gotland Sea during August and this maximum is also persistent during April, (Tables 1 and 2 and Fig. 3). The minimum ratio of ^{129}I -iodide/ ^{129}I -iodate is normally below 1, as observed for the ^{127}I -iodide/ ^{127}I -iodate, and occurs within the Skagerrak–Kattegat Basins.

Other interesting results in the surface waters are the ratios between the two isotopes species (Fig. 4). In both sampling campaigns, the ^{129}I -iodide/ ^{127}I -iodide values are decreasing going from the Skagerrak into the Baltic Proper, except for sample in August which show a rather low ratio in the north part of Skagerrak (Fig. 4a and c). For the ^{129}I -iodate/ ^{127}I -iodate, the gradual decrease from the Skagerrak

to the Baltic proper is apparent in the two sampling campaigns, but also shows some areas that have values higher or lower than the general trend (Fig. 4b and d).

4. Discussion

4.1. Iodide and iodate in surface water of Skagerrak and Kattegat

Despite the limited number of sampling sites used here, the general trend in variability of iodide and iodate (^{129}I and ^{127}I) is, to a large extent, linked to water transport and environmental conditions. It is important to mention that $^{129}\text{I}^-$ and $^{129}\text{IO}_3^-$ concentrations (Tables 1 and 2) are 2–5 orders of magnitude higher than marine environment level of the pre-nuclear era (10^{-12} for $^{129}\text{I}/^{127}\text{I}$ ratio) (Hou et al., 2009). Previous studies (Hou et al., 2002, 2009; Aldahan et al., 2006, 2007; Alifimov et al., 2004; Yi et al., 2011) have shown that a part of ^{129}I released into marine environment from La Hague (France) and Sellafield (UK) reprocessing plants is transported to the North Sea by the Atlantic Current and a part of this enters the Baltic Sea through the Skagerrak and Kattegat Basins.

Earlier publication by Yi et al. (2011) on the distribution of total iodine isotopes along the same sampling sites analyzed here shows rather strong dependence of iodine distribution on type of water masses. More details are, however, exposed by using the chemical speciation of the iodine isotopes. The relatively gradual decrease of the total concentration of both isotopes (^{127}I and ^{129}I), from Skagerrak and northern Kattegat to the Baltic Sea indicated by Yi et al. (2011) seems to be partly confirmed by the chemical speciation (Figs. 2 and 3). We observe also complicated distribution patterns revealed by the speciation analysis suggesting a complex transport and mixing of the high salinity water of the North Sea with the relatively low salinity water of the Baltic Sea (Fig. 5a and c). Occurrence of strips or pockets of iodide-rich water within the generally low

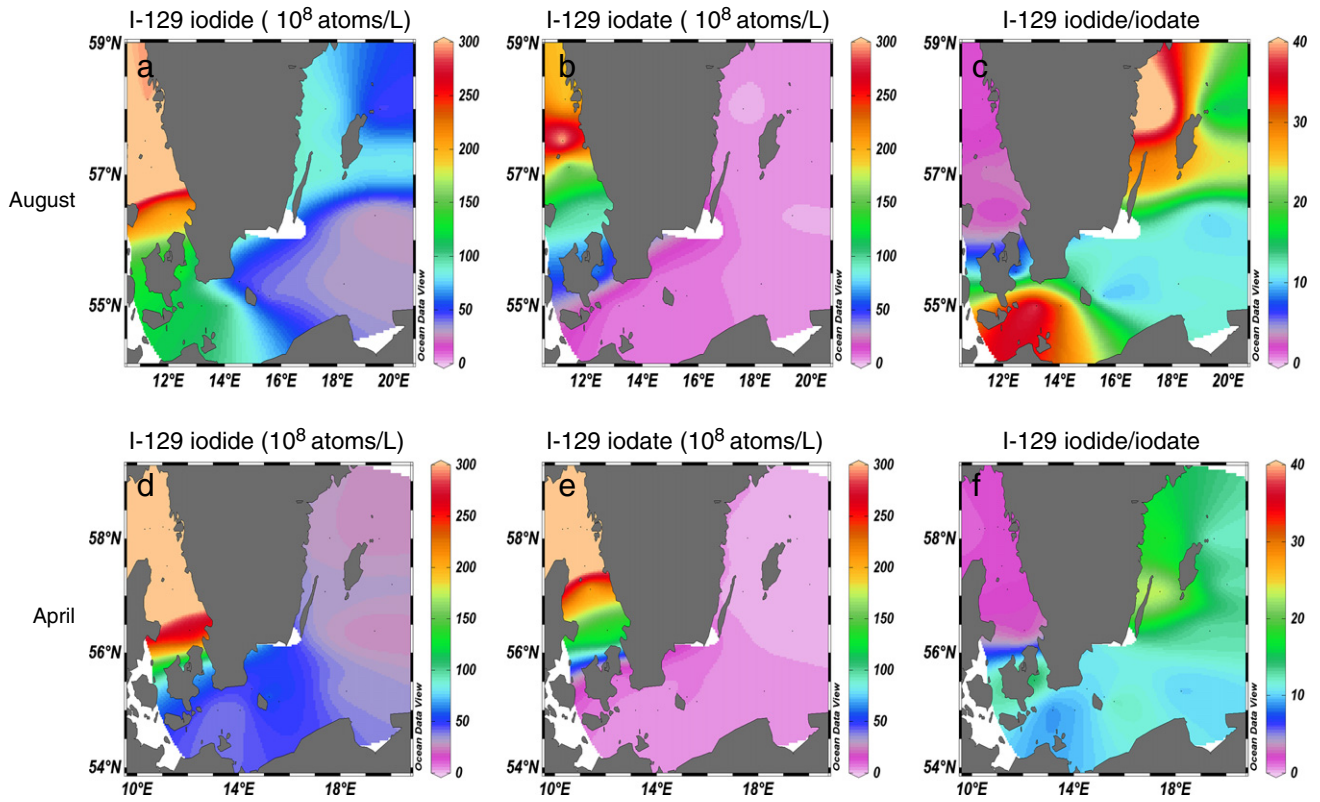


Fig. 3. Distribution of $^{129}\text{I}^-$, $^{129}\text{IO}_3^-$, $^{129}\text{I}^-/^{129}\text{IO}_3^-$ (a–f) in the surface water of Skagerrak, Kattegat and Baltic Sea for samples collected in August 2006 and April 2007.

regional trends in the Baltic Sea (Figs. 2c, f and 3c, f) suggests effect of upwelling anoxic deep waters that can be richer in iodide speciation.

Results presented here for speciation pattern of ^{129}I (Fig. 3) in surface water of the Skagerrak and Kattegat are comparable with data reported by Hou et al. (2007), suggesting that a large portion of ^{129}I as iodide and iodate in studied samples originate from North Sea. Data of surface water in the English Channel indicate ^{129}I -iodide as a predominate form, while in surface water of central and northern parts of the North Sea, relatively high concentrations of ^{129}I -iodide

were reported (Hou et al., 2007). In the present work a similar speciation pattern with relatively high iodide concentrations was found in all samples collected from Skagerrak–Kattegat basin which again reflect the effect of central and northern North Sea surface currents.

The correlation between iodide and iodate for ^{127}I is rather poor ($r^2=0.1$; Table 3), but it is better for the ^{129}I -iodide-iodate ($r^2=0.8$). Similarly good correlation is observed between salinity and ^{129}I species ($r^2=0.8$) whereas the relationship is less clear for the chemical speciation of ^{127}I . A poor correlation between the iodine

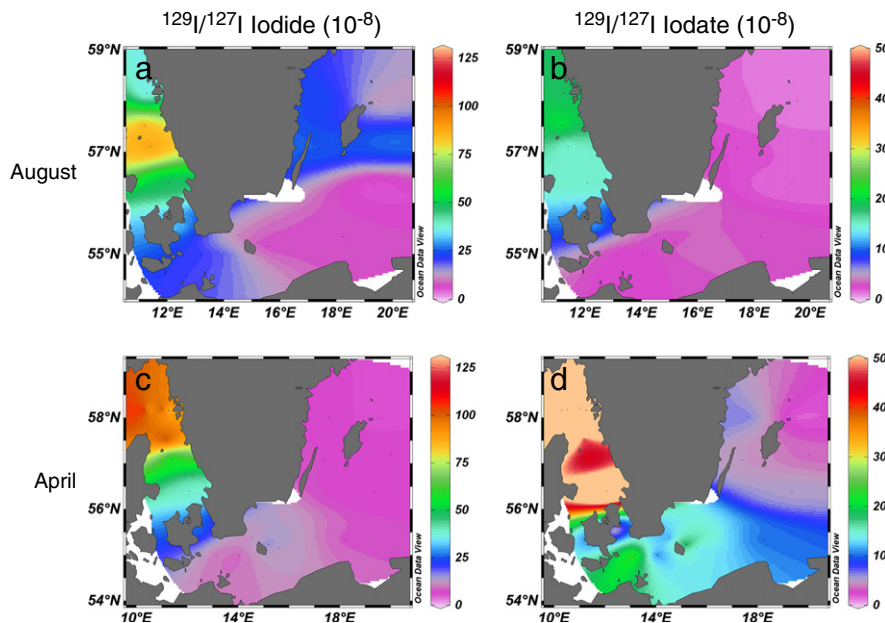


Fig. 4. Distribution of $^{129}\text{I}^-/^{127}\text{I}^-$, $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$ in the surface water of Skagerrak, Kattegat and Baltic Sea, during August 2006 and April 2007.

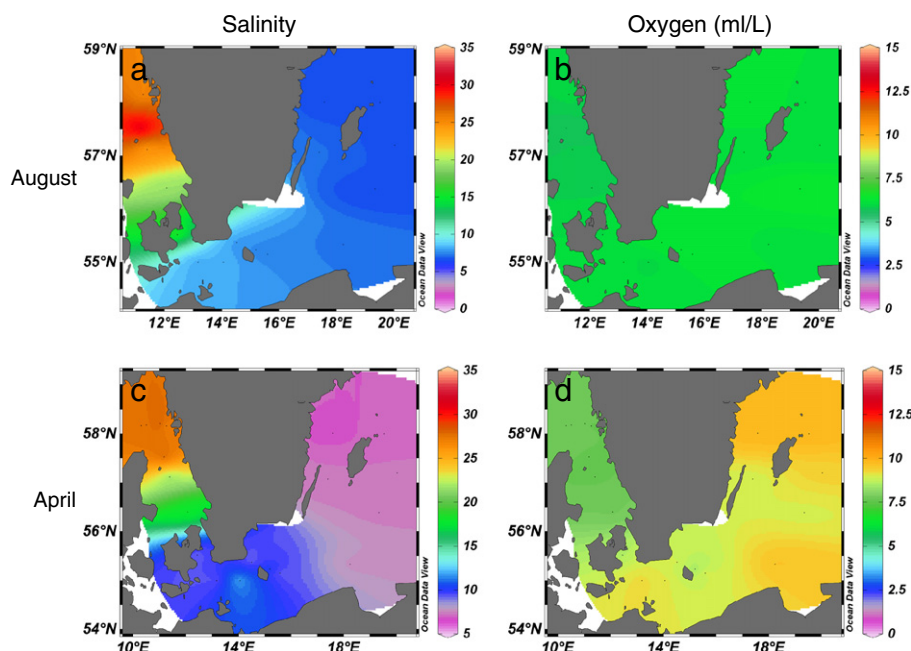


Fig. 5. Distribution of salinity and oxygen in the surface water of Skagerrak, Kattegat and Baltic Sea, during August 2006 and April 2007.

isotopes species and oxygen is observed (Table 3). These results suggest that the oxidation conditions of surface water do not influence the iodine speciation in the studied basins. This situation is also illustrated by Figs. 4 and 5, which show that despite rather uniform oxygen concentration in the surface water, there is a large variability in the iodine isotopes distribution. The different distribution pattern of iodide and iodate (^{129}I and ^{127}I) along the surface water of Skagerrak, Kattegat and Belt Sea (Fig. 1, station 12) is most likely due to the mixing process between saline North Sea-Atlantic and Baltic Sea fresher water (Figs. 2 and 3). North Sea surface water with high ^{129}I and ^{127}I iodide concentrations and high salinity (Hou et al., 2007) enters Skagerrak and mixes with the relatively low iodide concentrations (Figs. 2 and 3) and low salinity (Fig. 5) outflow waters from the Baltic Sea in the Kattegat through the Belt Sea (station 12, Fig. 1).

4.2. Iodide and iodate in surface water of Arkona Sea and Baltic Proper

In the Arkona Sea, higher $^{129}\text{I}^-/^{129}\text{IO}_3^-$ happened in August (Fig. 3c) and could be explained as a reduction of $^{129}\text{IO}_3^-$ along the water profile from Kattegat through the Belt Sea to $^{129}\text{I}^-$ as found along the surface water of southern Baltic Sea. However, ratio of $^{127}\text{I}^-/^{127}\text{IO}_3^-$, shows instead higher values in April (Fig. 2f), indicating a selective reduction of iodate that may be a significant process governing the out of equilibrium (freshly added to the environment) ^{129}I isotope compared to the naturally equilibrated ^{127}I isotope. As the Arkona Basin is end-member of relatively saline water, iodide and iodate concentration are severely affected by the mixing process.

Variability in the relative $^{129}\text{I}^-/^{127}\text{I}^-$ and $^{129}\text{IO}_3^-/^{127}\text{IO}_3^-$ values (Fig. 4) between the sampling campaigns (August-2006 and April-2007) can reflect seasonal and input effects. Addition of huge fresh

water to the system during spring snow and ice melting may preferentially alter the concentrations and iodine speciation, specifically in near coastal regions. During August, extensive algal blooming may on the other hand contribute to increase the iodide species, particularly near to coastal and shallow water regions. The present distribution of the studied sampling sites is rather limited and does not provide enough coverage to deduce specific distribution patterns of the isotopes in the surface water. Furthermore, addition of data on iodine speciation in depth profiles of the sampling site will expose better the interplay between regional water transport and environmental conditions. Nevertheless, the data presented here has shown for the first time the extent and general distribution patterns of iodine isotopes species that add new valuable information for future environmental analysis.

5. Conclusions

We here present data on iodine isotopes (^{129}I and ^{127}I) and their species (iodide and iodate) in surface water collected from 16 locations in August 2006 and 19 locations in April 2007 in the Baltic Proper, Kattegat and Skagerrak. From those results we draw the following conclusions: a) reduction of iodate and oxidation of iodide in Skagerrak and Kattegat may be a slow process since insignificant change in ^{129}I and ^{127}I speciation was found; b) reduction of iodate to iodide seems to be a relatively fast process in surface water of the southern Baltic Sea; c) oxidation conditions of the surface water are not exerting a marked effect on the iodine speciation in the studied basins; d) seasonal and input effects may alter the concentrations and speciation modes specifically in near coastal regions.

Acknowledgements

Funding for the sampling was provided by the Swedish Meteorological and Hydrological Institute (SMHI). We thank Lars Andersson and Bodil Thorstensson and all the crew and scientific team on board of the research vessel Argos for the help during the sampling expeditions. X.L. Hou appreciates the support by "BaiRen" Project of CAS (Grant No. KZCX2-YW-BR-13).

Table 3
Correlation relationship (R^2) between iodine species and oxygen and salinity.

	$^{127}\text{I}^-$	$^{127}\text{IO}_3^-$	$^{129}\text{I}^-$	$^{129}\text{IO}_3^-$	Oxygen	Salinity
$^{127}\text{I}^-$		0.14	0.44	0.52	−0.03	0.49
$^{127}\text{IO}_3^-$			0.37	0.36	−0.2	0.55
$^{129}\text{I}^-$				0.79	−0.08	0.8
$^{129}\text{IO}_3^-$					−0.04	0.75

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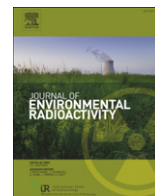
Paper IV

Hansen, V., Roos, P., Aldahan, A., Hou, X., Possnert, G. Partition of Iodine (^{129}I and ^{127}I) Isotopes in Soil and Sediment. *Journal of Environmental Radioactivity* xxx (2011) 1-9



Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvradPartition of iodine (^{129}I and ^{127}I) isotopes in soils and marine sedimentsVioleta Hansen^{a,*}, Per Roos^a, Ala Aldahan^{b,c}, Xiaolin Hou^a, Göran Possnert^d^a Risø National Laboratory for Sustainable Energy, NUK-202, Technical University of Denmark, Frederiksborgvej 399, P.O.B. 49, DK-4000 Roskilde, Denmark^b Department of Earth Science, Uppsala University, SE-758 36 Uppsala, Sweden^c Department of Geology, United Arab Emirates University, Al Ain, United Arab Emirates^d Tandem Laboratory, Uppsala University, SE-751 21 Uppsala, Sweden

ARTICLE INFO

Article history:

Received 16 May 2011

Received in revised form

12 July 2011

Accepted 19 July 2011

Available online xxx

Keywords:

Iodine-129, 127

Speciation

Iodine humic substances

ICP-MS

AMS

ABSTRACT

Natural organic matter, such as humic and fulvic acids and humin, plays a key role in determining the fate and mobility of radioiodine in soil and sediments. The radioisotope ^{129}I is continuously produced and released from nuclear fuel reprocessing plants, and as a biophilic element, its environmental mobility is strongly linked to organic matter.

Due to its long half-life (15.7 million years), ^{129}I builds up in the environment and can be traced since the beginning of the nuclear era in reservoirs such as soils and marine sediments. Nevertheless, partition of the isotope between the different types of organic matter in soil and sediment is rarely explored. Here we present a sequential extraction of ^{129}I and ^{127}I chemical forms encountered in a Danish soil, a soil reference material (IAEA-375), an anoxic marine sediment from Southern Norway and an oxic sediment from the Barents Sea. The different forms of iodine are related to water soluble, exchangeable, carbonates, oxides as well as iodine bound to humic acid, fulvic acid and to humin and minerals. This is the first study to identify ^{129}I in humic and fulvic acid and humin. The results show that 30–56% of the total ^{127}I and 42–60% of the total ^{129}I are associated with organic matter in soil and sediment samples. At a soil/sediment pH below 5.0–5.5, ^{127}I and ^{129}I in the organic fraction associate primarily with the humic acid while at soil/sediment pH > 6 ^{129}I was mostly found to be bound to fulvic acid. Anoxic conditions seem to increase the mobility and availability of iodine compared to oxic, while subaerial conditions (soils) reduces the availability of water soluble fraction compared to subaqueous (marine) conditions.

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1. Introduction

The bioavailability of radioactive pollutants in the environment plays a decisive role in relation to the environmental pollutant impact, and in particular to the internal and external doses to humans. The bioavailability of a pollutant is generally related to its speciation and accordingly, chemical species of radionuclides can be a determining factor affecting their environmental impact and hazard. Iodine-129 can also be released in reactor accidents due to its high volatility, and can in this context serve as a retrospective tracer shedding new light on the environmental behavior of the radiologically much more important, but also much more short-lived ^{131}I . Practices of speciation analyses for radionuclides are a relatively recent implement and the literature data are rather

scarce. The concentrations of the radioactive isotope ^{129}I have been and are still increasing in the environment since the beginning of the atomic era in the late nineteen forties (Hou et al., 2009a; Englund et al., 2010; Aldahan et al., 2007a; Lo'pez-Gutierrez et al., 2004). As iodine is a biophilic element its distribution in the environment merits investigation (Hou et al., 2003, 2009a; Aldahan et al., 2007a). The isotope has a half-life of (15.7 million years) and it is naturally formed by cosmic-ray-induced spallation of xenon in the upper atmosphere, spontaneous fission of ^{238}U and in minor quantities, by neutron bombardment of tellurium in the geosphere. Thermal neutron induced fission of ^{235}U is another minor natural source of ^{129}I in the lithosphere. Presently, the source of additional ^{129}I in the environment is mainly from human nuclear activity such as nuclear reprocessing facilities, nuclear weapons testing and accidents associated with nuclear power plants. Contributions of ^{129}I from nuclear weapon tests (57–63 kg of ^{129}I), the Chernobyl accident (1.3–6 kg of ^{129}I) and nuclear power plants are relatively insignificant (Hou et al., 2009a; Englund et al., 2010 and Andersson et al., 2009). Discharges from nuclear reprocessing facilities into the marine and atmospheric environments represent

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the greatest releases of ^{129}I (Hou et al., 2003, 2009a; Englund et al., 2010; Andersson et al., 2009). By 2007, respectively 3800 and 1400 kg of ^{129}I have been discharged into the English Channel from the La Hague reprocessing plant and to the Irish Sea from the Sellafield reprocessing plant (Hou et al., 2009a). During this time period, atmospheric releases from these plants have been 75 and 180 kg, respectively (Hou et al., 2009a).

Literature data (Englund et al., 2010; Hou et al., 2003; Schlegel et al., 2006; Sheppard and Thibault, 1992) have shown that iodine association with organic matter accounts for a large part of iodine pool in soil and sediments. Furthermore, the mobility of iodine in soil and sediments seems to be strongly dependent on the content and type of organic matter. A vertical increase in iodine concentration along an organic matter rich soil layer was found to be followed by a decrease as the amount of organic matter decreased (Aldahan et al., 2007a; Lo'pez-Gutierrez et al., 2004; Gallagher et al., 2005). Among the constituents of organic matter, humic substances (humic and fulvic acids as well as humin) play a key role in determining the fate and mobility of radioiodine in soil and sediments. Muramatsu et al. (1996) found that iodine sorption was not enhanced by adding nonhumified organic substances, such as straw and glucose, to a rice paddy soil. In an investigation related to the stability and mobility of ^{125}I labeled humic and fulvic acid in a glacial sand-groundwater system, Warwick et al. (1993) found that the fulvic acid which was extracted from groundwater and labeled with ^{125}I emerged from a 55 cm sand column. In the same experiment, Aldrich humic acid labeled with ^{125}I was more strongly sorbed in the columns of sand. The authors conclude that the mobility of a humic or fulvic material depends on the extent to which the available sites are already occupied.

Iodine mobility, environmental transport and biological uptake (Hou et al., 2009a; Andersson et al., 2009; Schlegel et al., 2006; Yamaguchi et al., 2006) greatly varies with iodine speciation and it is necessary to perform a chemical fractionation analysis in order to model its environmental behavior. Sequential extraction coupled with inductively coupled plasma mass spectrometry (ICP-MS) (Englund et al., 2010), X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure spectra (EXAFS) (Schlegel et al., 2006; Schulze and Bertsch, 1995; Feiters et al., 2005; Shimamoto and Takahashi, 2008; Kodama et al., 2006) have been used to determine stable iodine speciation in selected environmental samples. Using XANES and EXAFS techniques, the stable iodine is determined as iodide, iodate and organic matter associated iodine. Compared with stable iodine (^{127}I), the ^{129}I level in soil and sediment is often 4–12 (Hou et al., 2009a) orders of magnitude lower, which necessitates efficient extraction/enrichment and measurement techniques. The atomic spectroscopy based techniques mentioned above are not able to distinguish between isotopes, meaning that the speciation of much more abundant ^{127}I isotope would completely dominate the observations. Sequential extraction coupled with RNAA (Radiochemical Neutron Activation Analysis) (Hou et al., 2003; Schmidt and Aumann, 1995) or AMS (Accelerator Mass Spectrometry) (Englund et al., 2010) has been applied for chemical fractionation of ^{129}I in soil and sediment. The chemical fractionation methods have usually been based on the classical Tessier (1979) extraction

protocol where the element in question was related to water soluble, exchangeable, carbonate, oxide, organic, and mineral associated forms. Sequential extraction procedure is somewhat problematic since different results can be obtained, even when using the same method but conducted in different laboratories (Hou et al., 2009b). This observation might be attributed to different detailed operational conditions as well as crossover between fractions which is not avoidable. However, the amount of iodide, iodate and organic iodine determined in soil samples by XANES were fairly consistent with the results indicated by sequential extraction (Kodama et al., 2006; Shimamoto et al., 2011).

Although a number of works on the speciation analysis of stable iodine in soil and sediments samples are reported, data on ^{129}I speciation in soil and sediment are still scarce. To the best of our knowledge the specific association of ^{129}I to humic acid, fulvic acid, and humin has not been reported earlier.

Here we present a speciation analysis method for ^{129}I and ^{127}I in soil and sediment, to identify different iodine fractions such as water soluble, exchangeable, carbonate, oxide, as well as associated to humic acid, fulvic acid, humin and unaffected mineral forms. In particular, we focus on investigating the iodine mobility and bioavailability and whether stable iodine and ^{129}I behave similarly in soil and marine sediment reservoirs, despite the relatively recent extensive addition of ^{129}I in the environment.

2. Materials

2.1. Reagents

Iodine carrier was prepared from low level iodine (Woodward company, USA). Analytical standards produced from solution of ^{129}I (NIST-SRM-4949c) were purchased from National Institute of Standard and Technology (NIST) (Gaithersburg, MD, USA). The standard was diluted with iodine carrier and used for calibration during AMS analysis. Carrier free ^{125}I (NaI form) was purchased from Amersham Biotech (UK). A ^{127}I standard was prepared using KIO_3 (analytical reagents, Merck, Germany). All other chemicals reagents used were of analytical reagent grade. All solutions were prepared using deionized water (18.2 M Ω , Sartorius Stedim Biotech system). Tetramethylammonium hydroxide (TMAH) solution (25%) was purchased from Sigma Aldrich.

2.2. Soil and sediment samples

A soil reference material (IAEA-375), a Danish soil, an anoxic sediment and an oxic sediment were used in this work. The sampling locations of the investigated samples are presented in Table 1. The reference material, IAEA-375, is a Chernobyl accident contaminated soil collected from Bryansk, Russia (Table 1) in 1990 and prepared and distributed by International Atomic Energy Agency (Vienna, Austria). The Danish soil was collected in the top 10 cm from 12 different locations in Denmark in 2003 (Table 1), and was dried, mixed, ground, and sieved through a 0.4 mm sieve to represent inter-comparison material. The anoxic sediment was collected from the upper 40 cm layer using a Kajak (handheld) type of sediment core sampler with 74 mm in diameter from South

Table 1
Information on analyzed samples in this work.

Sample	Depth (mm)	Location	Longitude	Latitude	Sampling date	Sample pH
Oxic sediment	20–30	Barents Sea	68° 52' 6" N	50° 06' 5" E	Aug. 1994	5.5
Anoxic sediment	400	Helvik Fjord, Norway	58° 04' 40" 56" N	6° 46' 31.10" E	Aug. 1994	7.5
Danish soil	0–100	—	—	—	July, 2003	5.5
375 IAEA soil	0–200	Brjansk, Russia	52° 49' 53.60" N	32° 44' 21.82" E	July, 1990	5.0

Norway (Table 1). CTD-casts with oxygen probe showed almost zero concentration when approaching 15 m depth and the muddy sediments were completely black with distinctive smell of sulphide. The oxic sediment was collected from an upper 2–3 cm layer using a Multiple Core (MUC) sampler (10 cm in diameter) from Barents Sea (Russia) (Table 1). For the Barents Sea sediment we have no evidence of that the entire part used was oxic but no black coloration was present.

After sampling, the oxic and anoxic marine sediments was immediately freeze dried and stored in sealed polypropylene containers until analysis.

Unfortunately no pore water sampling was done on the sediments used here. Based on the much higher porosity of the anoxic fjord sediments and the lack of bioturbation it may be anticipated that the upward moving pore water (due to diffusion and compaction of sediments) show a greater influence of older (pre-anthropogenic) iodine than the oxic Barents Sea sediments where frequent mixing of top sediments (Carroll et al., 2008) expose the upper sediments more often to relatively young seawater.

3. Analytical methods

3.1. Sequential extraction procedure

Iodine (^{127}I and ^{129}I) was sequentially extracted according to the scheme presented in Table 2.

The fractions 1–4 and 6 was extracted according the procedure of Hou et al. (2003) while the organic matter fraction was extracted following the procedure presented by Yamada et al. (1999). Further separation of humic and fulvic fractions was performed according to the classical method (Schnitzer and Khan, 1978). Leaching solutions were added in a sample/solution ratio of 10 (v/w) in each step. After extraction, the leachate was separated by centrifugation at $3000\times g$ for 10 min. After removal of the supernatant, the remaining residue was rinsed with distilled water (18 M Ω /cm), in a water/sample ratio of 5 (v/w) by shaking the mixture for 10 min. The washes were combined with the leachate after centrifugation at $3000\times g$ for 10 min. The detailed procedure is presented below:

1. Water soluble fraction: 100 mL water was added to 10 g dry soil/sediment and the mixture was stirred for 1 h at 20 °C.
2. Exchangeable fraction: 100 mL of 1 M NH_4Ac –HAc (pH 7) was added to the residue from the step 1 and the suspension was stirred for 2 h at 20 °C.
3. Carbonate fraction: To the residue from the step 2, 100 mL of 1 M NH_4Ac (pH 5 adjusted using HAc) was added and the suspension was stirred for 2 h at 20 °C.
4. Metal oxide fraction: 100 mL of 0.04 M NH_2OH HCl (in 25 %HAc, v/v (pH 3) was added to the residue from the carbonate fraction. The suspension was stirred for 6 h at 80 °C.
5. Humic and fulvic acid fraction: 100 mL of 5% TMAH was added to the residue from step 4 and the mixture was stirred for 4 h at room temperature. The leachate was separated from the residue by centrifugation at $3000\times g$ for 30 min. The residue

was washed with 100 mL distilled water for 10 min while stirring, and the washing solution separated from the residue by centrifugation during 10 min at $3000\times g$ was combined with the leachate. A 2-mL aliquot of the leachate was taken for determination of total ^{127}I in organic fraction. The remaining leachate was acidified with H_2SO_4 to pH 1.5 and the solution was allowed to stand for 30 min and then centrifuged at $4200\times g$ for 30 min to separate the humic acid (precipitate) from fulvic acid (in solution). Two mL of this supernatant solution was taken for determination of ^{127}I bound fulvic acid. Iodine bound humic acid was calculated as the difference between iodine bound to fulvic acid and the total iodine in the TMAH leachate. The humic and fulvic acid fractions were freeze dried and ^{129}I in these fractions was separated by combustion method (see 3.2.1).

6. Residue fraction: The residue from step 5, was freeze dried and the iodine in this fraction was separated by combustion method (see 3.2.1).

3.2. Separation and determination of ^{129}I and ^{127}I

3.2.1. Fulvic/humic acids fractions and extraction residues

To the remaining residue and the humic and fulvic acid fractions, 100 Bq of ^{125}I tracer was added. Iodine in these samples was then separated by combustion at temperature $>800^\circ\text{C}$, using a combustion facility (Carbolite, UK). The released iodine, as I_2 , was trapped in alkali solution (0.4 M NaOH, 0.025 M $\text{K}_2\text{S}_2\text{O}_5$).

3.2.2. Separation of iodine from leachate

After taking 2 mL of each leachate and the trapping solution from the combustion for the determination of ^{127}I , 2.0 mg of ^{127}I carrier (Woodward iodine) and 0.5 mL of 1.0 M KHSO_3 were added. An ^{125}I tracer, 100 Bq, was added to all the fractions, except the trapping solution from combustion where ^{125}I already had been added. The solution was acidified to pH2 with 3 M HNO_3 , and the iodine was extracted using CCl_4 after addition of NaNO_2 to oxidize iodide to I_2 . The extraction was repeated and the CCl_4 phases were combined. The iodine in the CCl_4 was back-extracted in KHSO_3 solution. The extraction and back extraction was repeated to purify iodine.

3.2.3. ^{129}I preparation for AMS measurements

Iodine as iodide in the final back-extracted solution was transferred to a centrifuge tube, and 1.5 mL of 3 M HNO_3 was added. To the solution 1 mL of 1 M AgNO_3 was added and mixed. The AgI precipitate was separated by centrifugation for 4–5 min at $2500\times g$. The precipitate was washed with 1 mL distilled water and the supernatant was discharged after the centrifugation ($2500\times g$ for 4–5 min). The AgI precipitate was finally dried at 60–70 °C, and then ground to powder. After mixing with Niobium powder, the AgI samples were pressed into a copper holder and the measurement of $^{129}\text{I}/^{127}\text{I}$ ratios was carried out using the AMS system at the Tandem Laboratory, Uppsala University (5 MV Pelletron, National Electrostatic Corporation, USA) at a terminal voltage of 3.5 MV. The ^{129}I

Table 2
Sequential extraction procedure used in this work.

Speciation	Extracting Reagents	Temperature (°C)	Contact Time (h)	pH
Water soluble	Water	RT	1	soil/sediment
Exchangeable	1 M NH_4Ac –HAc	20	2	soil/sediment
Carbonate	1 M NH_4Ac –HAc	20	2	5
Oxides	0.04 M NH_2OH HCl	80	6	3
Humic and Fulvic acid	5% TMAH	RT	4	14
Humic and minerals	Residue			

RT: Room temperature, Ac: acetate, TMAH: tetramethylammonium hydroxide.

NIST-SRM-4949C standard with $^{129}\text{I}/^{127}\text{I}$ ratio of 1.1×10^{-11} was used. Blank samples were prepared using the same procedure as for samples for total iodine, iodide and iodate. The measured $^{129}\text{I}/^{127}\text{I}$ ratio in carrier blank samples ($1.5 \pm 0.5 \times 10^{-13}$) was two orders of magnitude lower than that in samples ($0.5\text{--}15 \times 10^{-11}$), and was subtracted from the measured value in the samples. Instrumental background for the AMS system was controlled by measurement of natural AgI (iodargyrite) crystal, which gave a $^{129}\text{I}/^{127}\text{I}$ ratio of 4×10^{-14} . The statistical error of the measurements at one standard deviation was $<10\%$.

3.2.4. ^{127}I preparation for ICP-MS measurements

For ^{127}I determination, 2 mL of the solutions from various fractions were diluted with 1% NH_3 to 20 mL, and Cs (as CsCl) was added as internal standard. The concentration of ^{127}I was determined using an X Series^{II} ICP-MS (Thermo Electron Corporation). The detection limit calculated as 3SD of blanks was 0.02 ng mL^{-1} for iodine.

4. Results

The distributions of ^{129}I , ^{127}I and $^{129}\text{I}/^{127}\text{I}$ in different fractions in the investigated samples are shown in Figs. 1 and 2 and Table 3. The concentrations of ^{129}I range at 0.04–0.8 mBq/kg for IAEA-375 soil, 0.02–0.6 mBq/kg for Danish soil, 0.007–0.3 mBq/kg for oxic sediment and 0.03–0.5 mBq/kg for anoxic sediment. The concentrations of ^{127}I ranged at 0.07–0.6 $\mu\text{g/g}$ for IAEA-375 soil, 0.1–1.8 $\mu\text{g/g}$ for Danish soil, 0.3–6.3 $\mu\text{g/g}$ for oxic sediment and 1.7–113.7 $\mu\text{g/g}$ for anoxic sediment. For IAEA-375 soil, the sum of ^{129}I concentration in all seven fractions (0.00197 Bq/Kg) agreed well with the reference value (0.0013–0.0021 Bq/Kg) within the analytical uncertainty.

The $^{129}\text{I}/^{127}\text{I}$ atomic ratios (Table 3, Fig. 2) ranged at (4.3×10^{-8} – 37.3×10^{-8}) for IAEA-375 soil, 0.5×10^{-8} – 9.2×10^{-8} for Danish soil, 0.4×10^{-8} – 1.8×10^{-8} for oxic sediment and

0.013×10^{-8} – 0.6×10^{-8} for anoxic sediment. Data for oxic sediment are all based on total mass, including salt while for anoxic sediment corrections were made for salt content. For the Barents Sea sediment this correction is very small, being only 1.7%.

In the anoxic sediment sample 45% of the total ^{129}I was found to be associated to the fulvic acid fraction while only 5% with the humic acid fraction (Fig. 1a). The corresponding association of stable iodine was 30% to the humic acid fraction and 16% to the fulvic acid fraction. Thus a different association pattern was shown for the two iodine isotopes. Results from the oxic sediments show that 21–32% (Table 3 and Fig. 1b) of both ^{127}I and ^{129}I extracted from oxic sediment was associated to the humic acid fraction and 9–10% to the fulvic acid fraction.

In the anoxic and oxic sediments, approximately 42–44% of ^{127}I was bound to humin and residue, while only 12–22% of ^{129}I (Table 3 and Fig. 1a,b) remained in this fraction.

The readily available fractions (water soluble and exchangeable fractions) contained only 2–5% of the total stable iodine and 3–12% of the total ^{129}I in both sediments (Fig. 1a,b and Table 3). A considerable amount of ^{127}I (10–20%) and ^{129}I (24–32%) (Table 3) was observed in the metal oxides associated fraction for both sediments.

Approximately 83–90% of the total ^{129}I in the two investigated soils was associated with oxides, humic and fulvic acid (Table 3 and Fig. 1c,d), while a small percentage ^{129}I ($<17\%$) existed in other fractions, i.e. water soluble, exchangeable, carbonate, humin and minerals fractions. Approximately 43–49% of total ^{129}I in the organic fraction was associated with humic acid while only 10% remained in the fulvic acid in the two investigated soils. In the two soil samples, 38–40% of the total ^{127}I was associated with humic acid, 11–17% with fulvic acid, and 16–18% with oxide, summing up to a total 65–75% of ^{127}I (Fig. 1c,d). Whereas 3–18% of ^{127}I was associated with humin and minerals fraction, and 11–22% existed as readily available fraction, i.e. water soluble and exchangeable form.

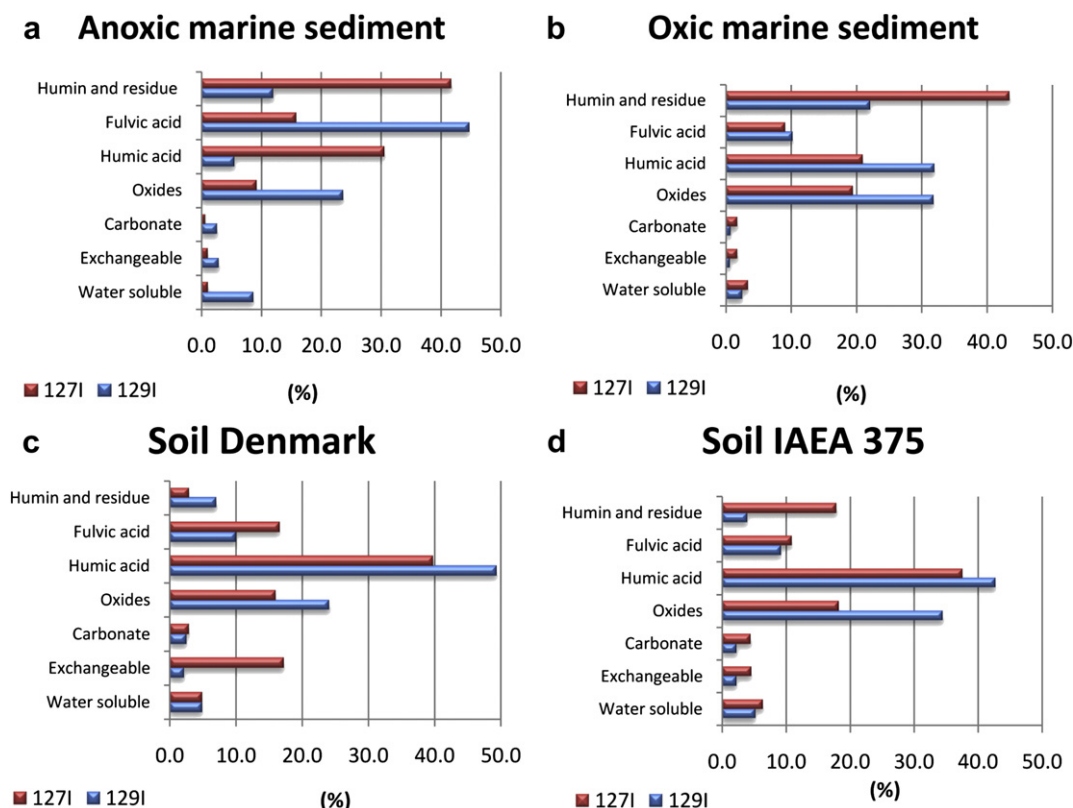


Fig. 1. Distribution (%) of ^{129}I and ^{127}I in the anoxic and oxic marine sediment, soil Denmark and IAEA-375 soil.

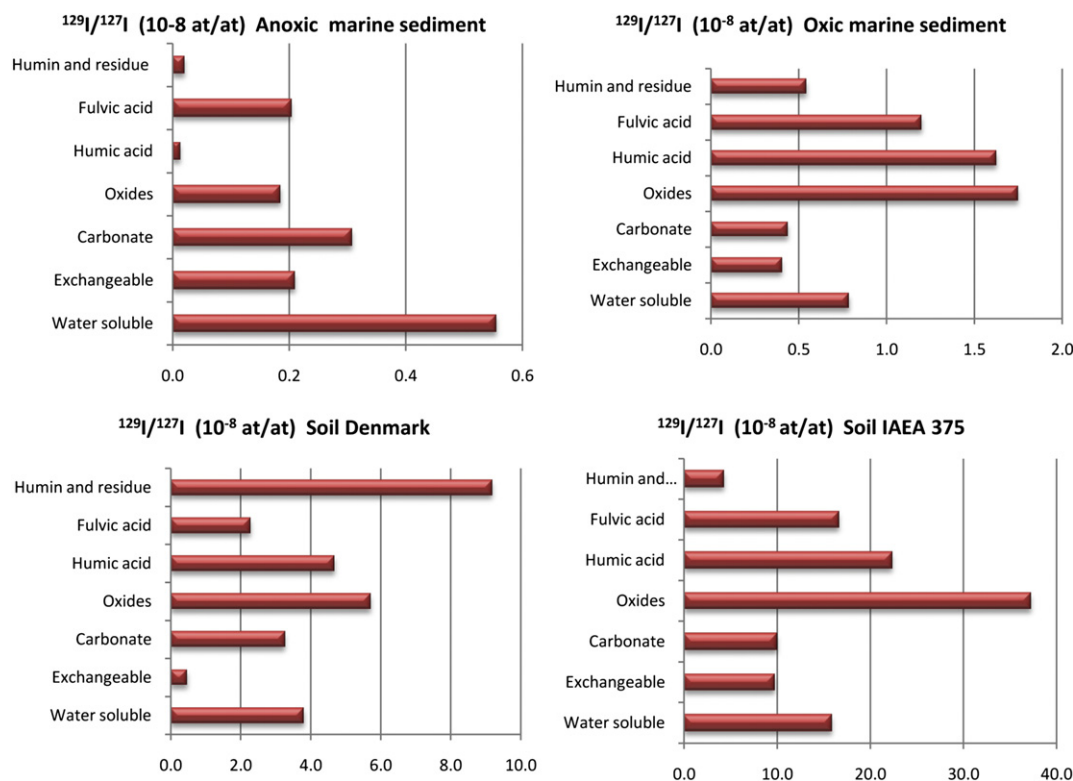


Fig. 2. Distribution of $^{129}\text{I}/^{127}\text{I}$ atomic ratios in the anoxic and oxidic marine sediment, soil Denmark and IAEA-375 soil.

5. Discussion

5.1. Separation of humic substance associated ^{129}I

A number of modified sequential extraction procedures originally proposed by Tessier (1979) has been reported and applied for investigation of association of ^{129}I in different components in soil and sediment samples (Englund et al., 2010; Hou et al., 2003; Schmidt and Aumann, 1995). However, none of these procedures allow identifying humic acid, fulvic acid and humin associated ^{129}I . Organic matter likely plays a major role in the geochemical cycle of iodine and thus the organic form that iodine may be associated with, will highly influence the mobility and availability of this element in soil and sediment. It is therefore important to design operationally defined speciation experiments so that the organic matter fractions can be investigated separately.

The isolation of humic substances from soil and sediment is normally implemented by extraction with alkaline solution, for example NaOH (Simpson and Johnson, 2006; Gonzalez-Vila and Martin, 1985), mild extractants such as sodium pyrophosphate (Hutta and Gora, 2003), or a mixture of pyrophosphate and NaOH (Tonelli et al., 1997; Ceccanti et al., 1986) at different conditions. Moreover, an extraction time of more than 12 h (Gonzalez-Vila and Martin, 1985) is normally applied when using alkaline extraction (NaOH), and a low extraction yield of humic substances was obtained when mild extractants were applied (Stevenson, 1994; Shirshova, 1991) comparing with alkaline extraction.

In order to investigate the isolation of iodine bound to humic substances in soil and the optimal leaching time of this fraction, two different extractants were used in this work. The iodine bound to humic substance from Danish soil was extracted with 5% TMAH for 4 h and with 0.1 M NaOH for 12 h at room temperature, under

stirring. The total concentration of ^{127}I (3.98 $\mu\text{g/g}$ sample) was obtained through the combustion method and ICP-MS measurement (see 3.2.1). The concentration of ^{127}I in the leachate was directly measured by ICP-MS and the results show a slightly higher amount (53% of total ^{127}I) in the leachate of 5% TMAH compared to that of 0.1 M NaOH which gave a value of 42%.

The humic substances in soils and sediments arise from the chemical and biological decomposition of plants and animal residues. Several studies (Schlegel et al., 2006; Reiller et al., 2006) effectuated on soils and marine sediments showed that the iodine is covalently bonded to humic and fulvic acid extracted from soil and sediments.

Oxidation and hydrolysis of humic substances may occur while leaching with basic extractants and thus the loss of iodine can be expected. Possible loss of iodine from humic acid during the leaching process due to the 5% TMAH was investigated. Humic acid (HA) extracted from soil/sediments and HA purchased from Sigma Aldrich was labeled with ^{125}I via electrophilic substitution using Chloramine-T. Following the labeling procedure, the iodine were covalently bonded to humic acid (Lassen and Carlsen, 1994). The recovery of ^{125}I in the humic acid after labeling was 98–99%. The labeled HA was then mixed with 5% of TMAH and stirred for 30 min. After precipitation of HA and centrifugation, the ^{125}I recovery in the ^{125}IHA were 95–99%. This result indicates that there is no significant loss of ^{129}I when 5% TMAH is used to extract the organic matter. Further the amount of organic iodine determined in soil samples by sequential extraction (using basic extractant) were consistent with the results of XANES (Kodama et al., 2006; Shimamoto et al., 2011).

The excellent recovery and short extraction time (4 h) using 5% TMAH compared with using NaOH (12 h), favors the use of this reagent to isolate the iodine bound to organic matter from the studied samples.

Table 3
Analytical results of ^{127}I , ^{129}I speciation in soil and marine sediment samples.

Fraction	¹²⁷ I		¹²⁹ I		¹²⁹ I/ ¹²⁷ I
	Concentration, µg/g	Distribution,%	Concentration, mBq/kg	Distribution %	10 ⁻⁸ ,at/at
Anoxic Marine Sediment					
Water soluble	3.1 ± 0.3	1.1 ± 0.003	0.1 ± 0.02	8.6 ± 1.5	0.6 ± 0.05
Exchangeable	2.7 ± 0.6	1.0 ± 0.01	0.04 ± 0.003	2.9 ± 0.2	0.2 ± 0.05
Carbonate	1.7 ± 0.2	0.6 ± 0.003	0.03 ± 0.01	2.6 ± 0.4	0.3 ± 0.03
Fe–Mn oxides	25.0 ± 6.7	9.3 ± 0.01	0.3 ± 0.05	23.6 ± 4.04	0.2 ± 0.05
Humic acid	79.4 ± 19.7	29.6 ± 0.01	0.07 ± 0.01	5.5 ± 0.6	0.01 ± 0.003
Fulvic acid	43.0 ± 7.8	16.0 ± 0.01	0.58 ± 0.1	44.7 ± 12.1	0.2 ± 0.03
Humin and residue	113.7±	42.3±	0.16 ± 0.02	12.0 ± 1.8	0.02±
Sum	268.5 ± 35.4	100.0 ± 0.04	1.3 ± 0.2	100.0 ± 20.7	
Total (combustion)	319.7±		NM		NM
Oxic marine sediment					
Water soluble	0.5 ± 0.1	3.4 ± 0.1	0.03 ± 0.01	2.5 ± 0.9	0.8 ± 0.1
Exchangeable	0.3 ± 0.1	1.8 ± 0.2	0.01±	0.7±	0.4 ± 0.1
Carbonate	0.3 ± 0.02	1.8 ± 0.1	0.01 ± 0.001	0.7 ± 0.1	0.4 ± 0.03
Fe–Mn oxides	2.8 ± 0.6	19.5 ± 0.1	0.3 ± 0.02	31.8 ± 1.8	1.7 ± 0.4
Humic acid	3.0 ± 0.9	21.0 ± 0.2	0.3 ± 0.05	31.9 ± 5.0	1.6 ± 0.5
Fulvic acid	1.3 ± 0.5	9.1 ± 0.3	0.1±	10.2±	1.2±
Humin and residue	6.2±	43.5±	0.2 ± 0.09	22.1 ± 8.9	0.5±
Sum	14.4 ± 24	100.0 ± 1	1.0 ± 0.2	100.0 ± 16.7	
Total (combustion)	19.7±		NM		NM
Danish Soil					
Water soluble	0.2 ± 0.05	4.8 ± 0.4	0.1 ± 0.01	4.9 ± 0.5	3.8 ± 0.7
Exchangeable	0.8 ± 0.2	17.2 ± 0.6	0.02 ± 0.01	2.1 ± 0.4	0.5 ± 0.1
Carbonate	0.1 ± 0.04	2.9 ± 0.5	0.03 ± 0.01	2.5 ± 0.4	3.3 ± 0.8
Fe–Mn oxides	0.7 ± 0.1	15.9 ± 0.3	0.3 ± 0.02	24.1 ± 1.4	5.7 ± 0.9
Humic acid	1.8 ± 0.2	39.8 ± 0.2	0.6 ± 0.2	49.3 ± 19.5	4.7 ± 0.5
Fulvic acid	0.8 ± 0.1	16.5 ± 0.2	0.1±	10.0±	2.3±
Humin and residue	0.1±	2.9±	0.1 ± 0.01	7.0 ± 0.6	9.2±
Sum	4.6 ± 0.8	100.0 ± 2.2	1.2 ± 0.3	100.0 ± 22.9	
Total (combustion)	4.0±		NM		NM
IAEA-SRM-375 soil					
Water soluble	0.1 ± 0.01	6.4 ± 0.2	0.1 ± 0.01	5.2 ± 0.4	15.9 ± 0.4
Exchangeable	0.1 ± 0.002	4.5 ± 0.03	0.04 ± 0.01	2.2 ± 0.7	9.7 ± 0.05
Carbonate	0.1 ± 0.02	4.5 ± 1.3	0.05 ± 0.01	2.3 ± 0.3	10.0 ± 1.9
Fe–Mn oxides	0.3 ± 0.07	18.2 ± 1.5	0.7 ± 0.3	34.5 ± 15.0	37.3 ± 8.3
Humic acid	0.6 ± 0.2	37.6 ± 1.6	0.8±	42.7±	22.3±
Fulvic acid	0.2 ± 0.02	10.9 ± 0.4	0.2±	9.2±	16.6±
Humin and residue	0.3±	17.9±	0.1 ± 0.004	3.9 ± 0.2	4.3±
Sum	1.7 ± 0.3	100.0 ± 5.0	2.0 ± 0.3	100.0 ± 16.5	
Total (combustion)	1.46±		NM		NM

*NM: not measured; concentrations of ^{127}I and ^{129}I in each component are in $\mu\text{g/g}$ – sediment/soil and mBq/kg – sediment/soil, respectively.

5.2. Partitioning of ^{129}I and ^{127}I

Iodine is an element with multiple oxidation states $-1, 0, +1, +3, +5$ and $+7$, forming a wide variety of chemical compounds in natural environmental Eh–pH conditions (Hou et al., 2009a; Liu and Gunten, 1988). In aqueous systems predominantly as iodide (-1) and iodate ($+5$) with a minor amount of organic iodine in seawater but considerable amounts in freshwater systems (Hou et al., 2009a; Wong, 1991; Wong and Zhang, 2003). Under anoxic conditions, aqueous iodine is predominant as iodide while under more oxidizing environments iodate is the inorganic predominant species (Hou et al., 2009a; Yuita, 1992; Yuita et al., 2005). In soils/sediments iodine occurs as organic and inorganic species (Hou et al., 2003; Englund et al., 2010; Schlegel et al., 2006; Sheppard and Thibault, 1992). Results of speciation analysis in such reservoirs reveal that a considerable part of iodine is adsorbed on oxides and hydroxides of iron and manganese (Hou et al., 2003, 2009a; Englund et al., 2010; Sheppard and Thibault, 1992) and most of iodine being associated with organic matter (Hou et al., 2003, 2009a; Englund et al., 2010; Schlegel et al., 2006; Sheppard and Thibault, 1992).

Soil and sediments may contain a large amount of organic matter which can be grouped into humic and non-humic substances. On the other hand, humic substances as humic acid (generally of high molecular weight), fulvic acid (generally of low molecular weight) and humin (condensed high molecular weight

organic matter with high C/N ratio and which is usually strongly adsorbed on minerals) (Schnitzer and Khan, 1978), are relatively more stable when comparing with non-humic substances in such reservoirs. Iodine may then find its way to humic substances in soils and sediments through: i) iodination of phenolic moieties through electrophilic substitution of hydrogen by an iodine atom on a phenolic ring (Hou et al., 2003; Lee, 1967), ii) iodination of amines (Brezonik, 1994), iii) methylation of inorganic iodine by biomass (Tessier et al., 2002), iv) iodination of thiol groups in proteins (Jirousek and Pritchard, 1971) has also been recently reported. Results from X-ray absorption spectroscopy (Schlegel et al., 2006) and X-ray photoelectron spectroscopy (XPS) (Reiller et al., 2006) confirm that iodine is mainly covalently bonded to natural organic matter such as humic and fulvic acid extracted from soil and sediments. Moreover, laboratory studies were performed with the aim of understanding the transformation of inorganic iodine into humic substances. Francios (1987) studied the uptake of iodine by humic substances extracted from marine sediments and concluded that under slightly acid conditions the iodate was reduced to an electrophilic species, i.e., $\text{I}_2(\text{aq})$ or HIO by sedimentary humic substances and reacts substantially with it while iodide does not. Fixation of iodide by humic substances was also investigated by Rädlinger and Heumann, (2000) and their results showed that the transformation of inorganic iodide into humic substances was enhanced by microorganisms.

In the present study 40–60% of ^{129}I and 30–50% of ^{127}I , was observed to associate with soluble humic and fulvic acids (Fig. 1 and Table 3).

Our results are in agreement with previously published data (Hou et al., 2003, 2009a; Englund et al., 2010; Schlegel et al., 2006; Sheppard and Thibault, 1992) supporting an association of iodine with organic matter in soils and sediments. Hou et al. (2003) investigated the fractionation of ^{129}I in soil (from areas near Chernobyl) and marine sediment (Irish Sea). Their results showed that 39–47%, of the ^{129}I was associated with organic matter. It was also reported that 73% of the ^{127}I and 66% of the ^{129}I was bound to organic matter in lake sediment collected in central Sweden (Englund et al., 2010). In contrast, it was reported that only 2–4% of the ^{127}I and 4–14% of the ^{129}I associated with organic matter, and 38–49% of the ^{129}I and only 2–4% of ^{127}I was water soluble in soil near the reprocessing facility in Karlsruhe (Germany) (Schmidt and Aumann, 1995). It is not clear why such differences exist, but it may be related to different residence (contact) time, pH, Eh, quantity and quality of organic matter, microbiological activity, soil matrix composition itself as well as differences in contaminant origin and chemical speciation of both isotopes deposited on the soil/sediment.

In the investigated samples, except the anoxic sediment, the ^{127}I and ^{129}I associate primarily with humic acid (Fig. 1). In the anoxic sediment approximately 45% of the total ^{129}I underwent sorption to low molecular fulvic acid (water soluble in both sides of pH scale), while an insignificant amount (5.5%) was found in the humic acid fraction (Fig. 1a). For the stable iodine, 16% (Table 3) of its total concentration was found in fulvic acid whereas 30% was associated with humic acid. Due to the coastal and shelf location of the studied sediment, a large part of the organic matter is of terrestrial origin and thus the different associations of stable iodine and ^{129}I may be due to association to different types of original organic material (eg. plankton vs sediment organic matter).

To explain the preferential association of iodine with humic and fulvic acid in the studied samples we should consider the pH of soils and sediments. At a pH 5.0–5.5 (Tables 1 and 3) the iodine associates primarily with the more compacted humic acid (which precipitate at a low pH) whereas at a pH > 6 iodine primarily associates with fulvic acid. Similar results were reported by Sheppard and Thibault (1992), where stable iodine was associated mostly with fulvic acid in sphagnum peat soil having a pH of 6.4 and with a humic acid in a Brunisol litter having a pH of 5.2. Fuge (1996) show that iodine were much enriched in soils with neutral to slightly basic than in acidic soils.

The large part (30–60%, Table 3) of total iodine (^{127}I and ^{129}I) bound to the organic matter fraction as well as the primary association of both iodine isotopes with humic acid at a soil/sediment pH below 6 (Table 1) and with fulvic acid at a sediment pH above 6 (Table 1) may indicate that the mechanism by which iodine is bound to organic matter is similar for both isotopes. Additionally iodine is most likely covalent bound to the humic substances in the investigated samples.

Considerable amounts of ^{129}I (24–35%) and ^{127}I (9–19%) (Fig. 1) were bound to the metal oxide fractions in all the samples studied. The interpretation of this is not so straightforward since often organic matter such as humic and fulvic acids are associated with metal oxides of iron and manganese. Several studies (Filius et al., 2000; Illés and Tombácz, 2006) have shown ready adsorption of large amounts of humic substances on soil metal oxides surfaces. This process is strongly influenced by the pH. Recently it was reported that the adsorption of humic substances on metal oxides surfaces decreases with increasing pH (Filius et al., 2000; Illés and Tombácz, 2006; Tipping, 1981). In this work a considerable percentage of ^{129}I and ^{127}I (Table 3) bound to the metal oxide

fraction in all studied samples may be due to adsorption of iodine associated humic substances on metal oxides surface. The anoxic sediment should be devoid in trivalently oxidized species of Fe and Mn, which are the more reactive oxides. The high fraction of oxides (Table 3) in the anoxic sediment could reveal possible changes that occur in speciation pattern of major elements of this sample during freeze drying and storage. Recent literatures have shown that freeze drying of anoxic sediment significantly decreased the iron concentration in exchangeable and carbonate fractions and increased the concentration of this element in oxide fraction (Rapin et al., 1986; Hjorth, 2004).

The relatively high amount of ^{127}I and ^{129}I found in the oxide fraction in the samples cannot be related only to adsorption of iodine humic and fulvic acid onto metal oxide surfaces. The adsorption capability of inorganic iodine species such as iodide and iodate to metal oxides has been widely investigated (Whitehead, 1974; Parfitt, 1978) and the results have shown that the sorption capacity decreases with increasing pH. Anoxic and oxic conditions may also have a significant role in the partition of iodine in soils/sediments. Under oxic condition, the IO_3^- has been found to be the predominant chemical species (Yuita, 1992; Yuita et al., 2005) in soil solutions while under anoxic conditions, both inorganic species of iodine as iodide and iodate, mainly as iodide was observed in soil solution (Yuita, 1992). It is well known that under anoxic soil/sediment conditions a lower E_h (reduction potential) develops and IO_3^- can be chemically reduced to I^- , which is also supported by the experiment in that the added IO_3^- to the anoxic soils was reduced to I^- (Yamaguchi et al., 2006). Due to the different conditions encountered in anoxic/oxic environment, iodide adsorption on metal oxide surfaces may predominates in anoxic sediment while in oxic sediment and the investigated soils the iodate adsorption onto metal oxides surface dominates among the inorganic iodine species.

5.3. Distribution of $^{129}\text{I}/^{127}\text{I}$ isotope ratio

Volatilization of molecular iodine and methyl iodide from surface seawater and oceans, atmospheric deposition and rock weathering are the primary sources of stable iodine in soil and sediments. If the long residence (contact) time of stable iodine in soils and sediments is taken into consideration, this isotope occupied the thermodynamically favorable sorption sites (Schmidt and Aumann, 1995) in such reservoirs. In contrast to stable iodine, ^{129}I represents a new addition to the present environment, which mainly originates from releases from reprocessing of spent nuclear fuel. The large amounts of ^{129}I released to the environment from reprocessing of spent nuclear fuel during the last decades have significantly raised the $^{129}\text{I}/^{127}\text{I}$ isotopic ratios in marine and terrestrial environments (Hou et al., 2009a; Englund et al., 2010). The reported natural isotopic ratio of $^{129}\text{I}/^{127}\text{I}$ is about 10^{-12} in terrestrial and marine environment (Hou et al., 2009a; Fehn et al., 2007). In the samples investigated here, values of $^{129}\text{I}/^{127}\text{I}$ isotopic ratios range at 10^{-6} – 10^{-8} , clearly indicating anthropogenic sources (Hou et al., 2003, 2009a; Englund et al., 2010; Aldahan et al., 2007a, 2007b; Lo'pez-Gutiérrez, 2004).

Further the bulk $^{129}\text{I}/\text{I}$ ratios resulting from dividing the totals (Table 3) of studied samples are 0.074×10^{-8} (anoxic marine sediment), 1.14×10^{-8} (oxic marine sediment), 3.9×10^{-8} (Danish soil) and 18.05×10^{-8} (IAEA-375 soil), fairly consistent with other studies. You et al. (1994) shows that for shallow seawater in the Barents, the ratio is 1.1×10^{-8} , essentially the same as that of shallow oxic sediment. Hou (2004), showed that $^{129}\text{I}/\text{I}$ ratios for lakes in Denmark ranged from $(2.5\text{--}27.3) \times 10^{-8}$, and for soils from Denmark got $(7.3\text{--}7.63) \times 10^{-8}$. Regarding the Chernobyl soil, Szidat et al. (2000) got 14×10^{-8} , Hou et al. (1999) got 17×10^{-8} ,

Marchetti et al. (1997) 12.7×10^{-8} , all similar to the bulk value of 18.05×10^{-8} . The Chernobyl soil $^{129}\text{I}/\text{I}$ ratio is not much higher than the iodine ratio for some Russian lakes (Reithmeier et al., 2007) that range from $(3.5\text{--}8.4) \times 10^{-8}$.

From our results 42–44% of ^{127}I is bound to the insoluble fraction, as humin and minerals, while only 12–22% of ^{129}I (Table 3 and Fig. 1a,b) remains in this fraction of the oxic and anoxic sediments. These results are noteworthy and reflect that the ^{127}I has been present much longer in those sediments than ^{129}I and therefore has been fixed more strongly to humin and minerals than ^{129}I which may be added to the sediment more recently and also from other sources than stable iodine. A similar observation was also reported for soil near the reprocessing facility in Karlsruhe (Germany) (Schmidt and Aumann, 1995) where a major part of stable iodine between 56 and 71% was strongly associated with the mineral fraction, while 8–26% of the total ^{129}I was recovered in this fraction, reflecting different sources and residence (contact) time of ^{127}I and ^{129}I .

Our data further show that the distribution of $^{129}\text{I}/^{127}\text{I}$ values differed significantly between phases (Fig. 2) and samples, indicating that equilibrium has not yet been reached for a large fraction of the released ^{129}I . This means that geochemical models based on stable iodine behavior cannot be used to trace the behavior of ^{129}I .

Relatively higher $^{129}\text{I}/^{127}\text{I}$ values were observed in the solid phase (oxides, humic acid, fulvic acid and humin and minerals, Table 3) of the Danish agricultural soil. In oxic sediment and soil reference material 375 IAEA, higher $^{129}\text{I}/^{127}\text{I}$ values (Table 3 and Fig. 2) were observed in oxide, humic and fulvic acid (Table 3). In the anoxic sediment the highest $^{129}\text{I}/^{127}\text{I}$ values ($0.3\text{--}0.6 \times 10^{-8}$) were observed in readily available fraction including water soluble, exchangeable and carbonate fractions, while lower values ($0.01\text{--}0.02 \times 10^{-8}$) were found in humic acid and humin and minerals fractions. Our results are in agreement with previous studies (Muramatsu et al., 1996; Muramatsu and Yoshida, 1999; Sheppard and Hawkins, 1995; Yuita, 1994) effectuated on anoxic/oxic soils which reveal a high desorption of radioactive iodine ^{125}I from soil solid phase to soil solution and low soil adsorption of new added ^{125}I under anoxic conditions when compared with oxic soils. Investigating the solid to liquid distribution coefficient, K_d , for iodine (^{125}I) in lake sediments, Bird and Schwartz (1996) found lower K_d , under anoxic when compared with oxic conditions. Their results also reveal higher sediment adsorption of new added ^{125}I in oxic conditions while an opposite trend occurs in anoxic environments.

On the background of the above and since the highest $^{129}\text{I}/^{127}\text{I}$ value was found in the readily available fraction it is concluded that the mobility and availability of ^{129}I in the anoxic sediment is markedly greater compared with oxic sediment and studied soils samples. Further, the primary association of ^{129}I with the low molecular weight fulvic acid which is water soluble through pH scale, is another evidence that the investigated anoxic sediment is not a particularly effective sink for long lived ^{129}I .

6. Conclusions

For the first time ^{129}I associated with humic and fulvic acid respectively and with humin in soil and sediments samples is reported.

The results of sequential extraction presented here point out that partition of ^{127}I and ^{129}I in soil and marine sediments agreed with results presented by other authors regarding association of large part of iodine in the organic fraction. Our data further indicated new findings about the partition of iodine within the organic fraction with respect to pH and oxygen conditions as well as the environmental situation. Within the organic fraction the isotopes

distribution seemed to be controlled by pH conditions where pH value below 5.0–5.5 promoted occurrence of ^{127}I and ^{129}I in the humic acid while at pH > 6 the partitioning was in the fulvic acid. Anoxic conditions seemed to increase the mobility and availability of iodine compared to oxic, while subaerial situation (soils) reduced the availability of water soluble fraction compared to subaqueous (marine) one. The enhanced mobility may be more of a problem in oxygen deficient salt marches, bog areas and flooded rice paddys than in otherwise oxic soils. The ^{129}I is still in disequilibrium in the studied reservoir suggesting that caution must be taken in the evaluation of radioactive iodine geochemistry in the environment.

Acknowledgements

VH is grateful to the Radioecology and Tracers Programme (headed by Sven P. Nielsen) at the Radiation Research Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, for supporting her Ph.D. project.

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Paper V

Hansen Violeta & Roos Per. 2011. Spatial and temporal variation of ^{129}I and ^{127}I by analysis of archived *Fucus Vesiculosus* samples from Denmark, Manuscript

Analysis of ^{129}I and ^{127}I in archived *Fucus Vesiculosus* samples from Denmark

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Abstract

Marine algae play an important role in the global cycle of iodine in the environment in the sense that they accumulate seawater iodine at high concentration levels and have the ability to transform iodine into volatile forms. In this study spatial and temporal trends in ^{129}I and ^{127}I concentrations in archived *Fucus Vesiculosus* samples collected from Rømø in the North Sea, Klint in the Kattegat, and Bornholm in the Baltic Sea have been evaluated using AMS and ICP-MS respectively. Concentrations of ^{129}I in *Fucus* from Rømø, North Sea proved to be at least one order of magnitude higher than concentration in *Fucus* from Bornholm, Baltic Sea. The ^{129}I content of *Fucus* increased significantly between 1986 and 2010. Yields ratios of $^{129}\text{I}/^{127}\text{I}$ (seaweed) relative $^{129}\text{I}/^{127}\text{I}$ (seawater) were found to be 0.5 for North Sea (2005), 0.7 (2006) for Southern Kattegat and 0.97 (2007) for Bornholm indicating that *Fucus Vesiculosus* can be used as bio-indicator organisms for iodine-129 in marine environment. Furthermore our data reveal that the iodide is more efficient to accumulate than iodate in *Fucus*.

Key words: ^{129}I , ^{127}I , *Fucus Vesiculosus*, alkaline digestion, AMS, ICP-MS, Baltic Sea, North Sea.

1. Introduction

Among iodine isotopes, ^{129}I has a half-life of 15,7 My and it is naturally formed by cosmic-ray-induced spallation of xenon in the upper atmosphere, spontaneous fission of ^{238}U in the geosphere and in minor quantities, by neutron bombardment of tellurium. Thermal neutron induced fission of ^{235}U is another minor natural source in the lithosphere. The reported natural isotopic ratio of $^{129}\text{I}/^{127}\text{I}$ is about 10^{-12} in terrestrial and marine environment (Hou et al., 2009; Fehn et al., 2007). Presently, the source of additional ^{129}I in the environment is mainly from human nuclear activity such as nuclear reprocessing facilities, nuclear weapons testing and accidents associated with nuclear power plants. Over the past decade, liquid and gaseous releases of ^{129}I from reprocessing facilities such as La Hague (France) and Sellafield (UK) has increased the natural environmental concentration by several orders of magnitude (Alfimov et al., 2004; Fehn et al., 2007; Aldahan et al., 2007). In the period 1999 - 2009, respectively 14.6 and 4.6 TBq of ^{129}I have been discharged into the English Channel from the La Hague reprocessing plant and to the Irish Sea from the Sellafield reprocessing plant (www.ospar.org).

It is well known that seaweed accumulates iodine from seawater and that the process depends strongly on seaweed type/species (Leblanc et al., 2006) as well as the region in which they are found (Shah et al., 2005). Furthermore marine algae play an important role (Leblanc et al., 2006) in the global cycle of iodine in the environment in the sense that they accumulate iodine as iodide (Kupper et al., 1998) from seawater and transform a part of it into volatile organic iodine (VOI), such as methyl iodide (CH_3I) or diiodomethane (CH_2I_2 ; Carpenter et al. 2007). Once released from the seawater surface the volatile organic iodine are broken down by photolysis and reactions with ozone (O_3) (Jones & Carpenter, 2005; Martino et al. 2006) forming a reactive pool of iodine species which afterwards contribute to the ozone depletion, particulates formation and cloud condensation nuclei formation (Küpper et al., 2008; O'Dowd

et al., 2002). Due to the fact that seaweed accumulate iodine from seawater at high concentration, they are considered excellent bio-indicators or long term integrators and they are often included in monitoring programs. Furthermore the relatively long half life of ^{129}I and long residence time (30 kyr) of iodine in the marine environment combined with the continuous releases from nuclear fuel reprocessing facilities make this isotope a suitable oceanographic tracer.

Despite the significant role of marine algae in the iodine cycle in the environment, there is still a lack in understanding the mechanism of iodine uptake in seaweed. It is well known that the major pool of iodine in seawater occur in two species, as iodide (I^-) or iodate (IO_3^-) with the latter predominantly found in open ocean water and the former in coastal waters with elevated organic matter or biological productivity. Considering seasonal effects on biological productivity it may be anticipated that this influences the relative proportions of the iodine species. If the magnitude of uptake of iodine in seaweed depends on the iodine speciation temporal variations in speciation may be visible in *Fucus* time trend data.

In this work we determined the concentrations of ^{129}I and ^{127}I and $^{129}\text{I}/^{127}\text{I}$ ratios in archived *Fucus Vesiculosus* samples collected from Rømø in the North Sea, Klint in the Kattegat, and Bornholm in the Baltic Sea from 2002 to 2010. The resulting data are evaluated in terms of spatial and temporal trends and the $^{129}\text{I}/^{127}\text{I}$ ratios are discussed. Furthermore the pattern of iodine accumulation in *Fucus* is also discussed.

2. Sampling and analytical methods

Reagents. All chemical reagents used were of analytical grade, and all solutions were prepared using deionized water ($>18.2\Omega$). A diluted ^{129}I standard (prepared from NISTSRM 4949C) with a $^{129}\text{I}/^{127}\text{I}$ ratio of 1.1×10^{-11} , ^{125}I tracer (Amersham Pharmacia Biotech, Little Chalfont, Buckinghamshire, UK), ^{127}I carrier (Woodward iodine, MICAL Specialty Chemicals, New Jersey) were used.

Samples and analytical methods.

Fucus Vesiculosus samples were collected from 2002 to 2010 from Rømø in the North Sea, Klint in the southern Kattegat, and Bornholm in the Baltic Sea. At Rømø, a total of 14 samples, about 1-4 samples per year were analyzed. At Klint, a total of 28 samples, about 2-5 samples per year were analyzed. At Bornholm, a total of 5 samples were analyzed. The seaweed samples were first dried, grounded and homogenized.



Fig. 1 Sampling locations for seaweed at Rømø, Klint and Bornholm

Around 0.1 g of sample was then taken and mixed with 5mL of 3M NaOH solution in a crucible and about 100 Bq of ^{125}I solution was added for chemical yield measurement. This mixture was dried at $70\text{--}80\text{ }^{\circ}\text{C}$, burned and ashed at $350\text{ }^{\circ}\text{C}$ for 30' and $650\text{ }^{\circ}\text{C}$ for 3h,

respectively. The iodine was leached from the ashed samples 100 mL of double distilled water at 100 °C and filtered. A known amount of the solution (0.1-0.5 mL) was removed for ICP-MS determination of ^{127}I and the remaining solution were subject to ^{129}I analysis. About 2.0 mg of stable iodine (prepared from Woodward iodine) was added to leached fraction as a carrier. To convert all iodine to iodide, 0.2 mL of 2.0 M NaHSO_3 was added and pH was adjusted to 2 using 3M HNO_3 . Iodine was first extracted with CCl_4 after oxidation of iodide to molecular iodine using NaNO_2 , and then again reduced and back-extracted using NaHSO_3 solution. The extraction and back-extraction step was repeated once to purify the iodine solution. The chemical yield of iodine in the whole procedure, measured by the added ^{125}I tracer, ranged from 56% to 70%.

^{127}I and ^{129}I preparation for ICP – MS and AMS measurement. The aliquot for ^{127}I was diluted to 10 - 25 mL with 0.1 M NH_4OH and stable Cs^+ as (CsCl) was added as an internal standard to a final concentration of 2.0 ng/mL. The concentration of ^{127}I was determined using an X SeriesII ICP-MS (Thermo Electron Corporation).

Iodine as iodide in the final back extracted solution was transferred to a centrifuge tube, and 1.5mL of 3M HNO_3 was added. To the solution 1mL of 1M AgNO_3 was added and mixed. The AgI precipitate was dried at 60-70 °C, and then ground to powder, mixed with niobium powder and pressed into a copper holder for measurements of ^{129}I by accelerator mass spectrometry (AMS) at the Tandem Laboratory, Uppsala University using a terminal voltage of 3.5MV. The statistical error of the analysis, including mainly measurement errors at 1 standard deviation was <10%. Blank correction was negligible.

3 Results

The concentrations of ^{129}I and ^{127}I and ratios of $^{129}\text{I}/^{127}\text{I}$ in the samples are listed in Tables 1-3. The concentrations of stable iodine (^{127}I , Tables 1-3) vary from 95 ug/g dry weight to 180 ug/g dry weight with a mean of 140 ug/g dry weight for samples collected from Bornholm in the Baltic Sea, 96 ug/g dry weight to 740 ug/g dry weight with a mean of 402 ug/g dry weight for samples collected from Klint in the southern Kattegat and 210 ug/g dry weight to 1100 ug/g dry weight with a mean of 505 ug/g dry weight for samples collected from Rømø in the North Sea. The monthly results at Rømø and Klint indicate that an increase of ^{127}I in *Fucus* occur mostly during autumn – winter (Figures 5 and 6). The data reveal that concentrations of I-129 in samples from Rømø are approximately one order of magnitude (Table 1) higher relative to samples from Bornholm (Table 3) during the period 2004 – 2010. The iodine - 129 concentrations in seaweed collected from Rømø from 2004 to 2010 vary between 1.8×10^{-10} to 1×10^{-9} while at Klint from 2002 to 2010 concentrations vary between 8.5×10^{-12} to 2.5×10^{-10} dry weight and at Bornholm from 2002 to 2010 vary from 9.9×10^{-12} to 1.7×10^{-11} . The results of the $^{129}\text{I}/^{127}\text{I}$ ratios for all samples are shown in Figures 2-4. The $^{129}\text{I}/^{127}\text{I}$ ratio ranged between 6.9×10^{-7} - 1.9×10^{-6} for seaweed from Rømø, 6.3×10^{-8} - 7.1×10^{-7} for seaweed collected from Klint and 6.0×10^{-8} - 1.2×10^{-7} for seaweed collected from Bornholm.

4 Discussion

Despite the limited number of sampling sites used here the concentrations of stable iodine (^{127}I) vary significantly (Tables 1-3 and Figures 2-4) with the lowest values founded at Bornholm in the Baltic Sea were 140 ± 40 ug/g (1 std, n=5) dry weight was obtained. At Rømø and Klint the I-127 concentrations ($505 \pm 230 \mu\text{g/g}$ and $402 \pm 190 \mu\text{g/g}$) were more or less the same. Large seasonal variations of stable iodine in seaweed samples have been reported before (Hou & Yan, 1998, Hou et al., 2000; Sash et al., 2005; Keogh et al., 2007) and are viewed as a result of variable uptake over the various physical parts of the plant, seasonal variations as well as due to slightly different sampling locations with different

salinities in the same area. Apart from these variables it may also be anticipated that the relative proportions of the two iodine seawater species, iodide and iodate, may influence the uptake in *Fucus*. We have earlier shown (Hou et al., 2007; Hansen et al., 2011, Yi et al., 2012 in work) that the dominating iodate species gradually is reduced to iodide while moving from the North Sea into the Baltic Sea.

Alternatively other biochemical factors such as differences in the amount of dissolved organic carbon or seawater composition (eg. salinity) between the locations may be responsible for the observed changes. It is well known (Hansen et al., 2011b) that iodine sticks to dissolved organic matter and may thus be less prone to accumulate in seaweed. Concentrations of DOC in the southern Baltic Sea are typically 1-2 orders of magnitude higher than in Kattegat and North Sea.

In contrast to stable iodine the concentrations of anthropogenic iodine (Iodine-129) are orders of magnitude higher in samples collected from Rømø in the North Sea compared with samples collected from Baltic Sea and southern Kattegat. Our results are in agreement with previously published data (Hou et al, 2000) supporting a clearly decreasing trend of iodine - 129 in *Fucus* from Klint to Bornholm. These results are expected given the proximity of Rømø to the La Hague reprocessing plant and previous observations on coastal currents in the south part of the North Sea. Dahlgaard et al (1995) estimated that roughly 10% of the La Hague (English Chanel) and 2% of the Sellafield (Irish Sea) releases are transported into Kattegat.

The relative decrease of seawater iodine-129 moving from the North Sea, Skagerrak towards the south parts of the Baltic Sea indicated by Hou et al., (2007) and Yi et al., (2011) seems to be partly confirmed by the iodine-129 level in *Fucus* (Tables 1-3). Due to the large variations of ^{129}I concentrations, the $^{129}\text{I}/^{127}\text{I}$ ratio is a more reliable index of the level of ^{129}I enrichment in seaweed (Hou et al., 2000; Keogh et al., 2007). It is important to mention that the ratios of

$^{129}\text{I}/^{127}\text{I}$ in all the samples investigated here are four – five orders of magnitude higher than the reported natural isotopic ratio of $^{129}\text{I}/^{127}\text{I}$ (10^{-12} , Fehn et al., 2007). The ratios of $^{129}\text{I}/^{127}\text{I}$ in Fucus from Rømø were found to be in order of 10^{-7} and 10^{-8} in Fucus from Bornholm. Those variations may be related to different factors as for example: i) Fucus from different locations have integrated the iodine signal over different periods of time meaning that the seaweed cannot be used as a monitor of water concentration, ii) short – term variations in the discharge of radioiodine from nuclear reprocessing plants, iii) variations in transfer factors from the two reprocessing plants in this case La Hague and Sellafield.

Even if fluctuating biological functions in seaweed may be compensated for by using the $^{129}\text{I}/^{127}\text{I}$ ratio the question still remains to what level the seaweed is reflecting an average seawater ratio. This question is particularly interesting if the uptake of iodine depends on what species it occurs in. Previous investigation (Hou et al., 2007; Hansen et al., 2011) have shown that the two isotopes does not distribute among the two species, iodate and iodide, in a similar way. This is an effect of the very slow kinetic exchange between iodide and iodate in seawater. Iodine-129 in the form of iodide may thus remain as iodide even when the coastal water from the English Channel mixes with more open ocean water where the main fraction of stable iodine, I-127, exist in the form of iodate. If steady state conditions occur and the iodine uptake in seaweed would be the same irrespectively of species the concentration factor defined as ratio of $^{129}\text{I}/^{127}\text{I}$ (seaweed) relative $^{129}\text{I}/^{127}\text{I}$ (seawater) should be one. Using existing $^{129}\text{I}/^{127}\text{I}$ data in seawater from North Sea, Kattegat and Baltic Sea (Hou et al., 2007, Hansen et al. 2011) and combining it with the $^{129}\text{I}/^{127}\text{I}$ data at corresponding years presented here yields ratios of 0.5 for North Sea (2005), 0.7 (2006) for Southern Kattegat and ~1 (2007) for Bornholm. Thus, the $^{129}\text{I}/^{127}\text{I}$ ratios in collected Fucus samples, closely match with corresponding data from water. The somewhat larger difference at Rømø may be an effect of this location being closer to the source and the relatively short residence time of water in the

North Sea. $^{129}\text{I}/^{127}\text{I}$ ratios in water at this location may be expected to have a larger short term variance than sites further away such as Kattegat and the south Baltic Sea. The $^{129}\text{I}/^{127}\text{I}$ ratios in water at Rømø may thus deviate more from the average concentration which is reflected in the Fucus data. The time period over which Fucus is integrating water iodine is not known. The seawater salinity at the three locations may also be the reason for the large difference in concentration factors. The salinity at the three locations is roughly 35 ‰ (Rømø), 18‰ (Klint) and 7‰ (Bornholm) respectively. Variation in concentration factors (Fucus to seawater ratios) between Fucus samples collected on the Swedish west and east coast were reported by Carlsson and Erlandsson (1991) for radiocesium where they observed *higher* concentration factors at lower salinity.

Furthermore studies conducted with the aim of understanding the mechanism of iodine uptake in brown seaweed have pointed out that oxidation of seawater iodide to more lipophilic species such as HIO and I_2 which finally are taken up by marine algae (Shaw 1959; Kupper et al., 1998). In seawater iodine exists mainly as iodide (-1), iodate (+5) and to a lesser extent as organic iodine (Wong and Zhang, 2003; Wong, 1991). Earlier publication by Hou et al., (2007) on the speciation pattern of ^{127}I in surface water of the North Sea (high salinity) near Rømø, indicate similar concentrations of iodide (0.126 μM) and iodate (0.121 μM). Results of Hansen et al., (2011) shows relatively high concentrations of ^{127}I -iodide in surface water of Kattegat basin near Klint and Baltic Sea, Bornholm. Using the speciation pattern of iodine (^{129}I and ^{127}I) in seawater in all three surveys and combining it with the values of $^{129}\text{I}/^{127}\text{I}$ (seaweed) relative $^{129}\text{I}/^{127}\text{I}$ (seawater) we conclude that the iodide is more efficient to accumulate than iodate in Fucus. The high enrichment of iodine in Fucus may however be explained not only by preferential uptake of iodide since a significant increase of ^{127}I in Fucus occur mostly in autumn – winter even different speciation of ^{127}I in all three investigated studies occur. Several factors such as various physical parts of the plant, salinity, temperature,

content of organic matter and nutrients concentration in seawater may also control the mechanism of iodine uptake in *Fucus*. Nevertheless, the data presented here has shown that the *Fucus Vesiculosus* may accumulate preferential iodine as iodide.

Further the releases of anthropogenic iodine from La Hague (France) and Sellafield (UK) reprocessing facilities are illustrated best by comparing the $^{129}\text{I}/^{127}\text{I}$ ratios in *Fucus* samples collected from all three surveys from 1986 to 2010 (Figs. 2-4).

Table 1 Analytical results of 129-Iodine and 127-Iodine concentrations in seaweed samples collected from Rømø, Denmark

Sampling location	Sampling date	Iodine-129 concentration (g g^{-1})	Iodine-127 concentration (g g^{-1})	$^{129}\text{I}/^{127}\text{I}$ ratio
Rømø	26-03-2004	2.9E-10	4.2E-04	6.9E-07
Rømø	16-06-2004	1.8E-10	2.1E-04	8.7E-07
Rømø	11-09-2004	4.3E-10	5.2E-04	8.1E-07
Rømø	02-12-2004	6.0E-10	6.1 E-04	9.7E-07
Rømø	1-4 kvt bulked 2005	4.0E-10	5.3E-04	7.4E-07
Rømø	1-4 kvt bulked 2006	4.4E-10	4.6E-04	9.3E-07
Rømø	1-4 kvt bulked 2007	3.2E-10	2.6E-04	1.2E-06
Rømø	14-12-2008	8.9E-10	1.1E-03	7.6E-07
Rømø	1-4 kvt bulked 2008	6.2E-10	4.6E-04	1.3E-06
Rømø	19-03-2009	3.4E-10	4.2E-04	8.1E-07
Rømø	11-06-2009	9.6E-10	5.0E-04	1.9E-06
Rømø	15-09-2009	1.0E-9	7.9E-04	1.3E-06
Rømø	18-03-2010	2.5E-10	3.2E-04	7.7E-07
Rømø	01-06-2010	4.6E-10	5.8E-04	7.8E-07

Table 2 Analytical results of 129-Iodine and 127-Iodine concentrations in seaweed samples collected from Klint, Denmark.

Sampling location	Sampling date	Iodine-129 concentration (g g⁻¹)	Iodine-127 concentration (g g⁻¹)	¹²⁹I/¹²⁷I ratio
Klint	12-03-2002	1.1E-10	4.7E-04	2.1E-07
Klint	14-06-2002	3.4E-11	1.5E-04	2.2E-07
Klint	12-09-2002	5.1E-11	2.4E-04	2.1E-07
Klint	05-12-2002	1.5E-10	7.5E-04	2.0E-07
Klint	02-03-2004	1.2E-10	5.9E-04	2.0E-07
Klint	06-12-2004	1.9E-10	7.4E-04	2.5E-07
Klint	18-03-2005	9.2E-11	2.9E-04	3.2E-07
Klint	07-04-2005	1.1E-11	1.7E-04	6. 3E-08
Klint	07-06-2005	6.4E-11	1.9E-04	3.2E-07
Klint	04-09-2005	5.7E-11	2.7E-04	2. 1E-07
Klint	07-12-2005	8.0E-11	3.6E-04	2.2E-07
Klint	06-03-2006	1.1E-10	3. 9E-04	2.7E-07
Klint	21-04-2006	8.5E-12	9.6E-05	8.8E-08
Klint	18-06-2006	7.0E-11	3.5E-04	1.9E-07
Klint	13-09-2006	1.1E-10	5.3E-04	2.1E-07
Klint	06-12-2006	1.3E-10	4.4E-04	2.9E-07
Klint	16-09-2007	1.6E-10	4.6E-04	3.3E-07
Klint	06-12-2007	2.2E-10	6.2E-04	3.5E-07
Klint	06-03-2008	1.3E-10	4.2E-04	3.2E-07
Klint	17-06-2008	1.5E-10	2.1E-04	7.1E-07
Klint	22-09-2008	5.4E-11	1.6E-04	3.2E-07
Klint	09-12-2008	1.9E-10	4.9E-04	3.9E-07
Klint	28-03-2009	9.6E-11	2.9E-04	3.3E-07
Klint	25-06-2009	1.2E-10	5.4E-04	2.3E-07
Klint	03-09-2009	7.7E-11	3.3E-04	2.3E-07
Klint	03-12-2009	1.6E-10	4.5E-04	3.5E-07
Klint	09-03-2010	2.5E-10	7.4E-04	3.3E-07
Klint	06-06-2010	1.1E-10	5.2E-04	2.1E-07

Table 3 Analytical results of ^{129}I -Iodine and ^{127}I -Iodine concentrations in seaweed samples collected from Bornholm.

Sampling location	Sampling date	Iodine-129 concentration (g g^{-1})	Iodine-127 concentration (g g^{-1})	$^{129}\text{I}/^{127}\text{I}$ ratio
Bornholm	03-04-2002	9.9E-12	1.6E-04	6.0E-08
Bornholm	18-04-2007	1.1E-11	1.2E-04	9.2E-08
Bornholm	05-04-2008	1.6E-11	1.8E-04	9.2E-08
Bornholm	16-04-2009	1.7E-11	1.5E-04	1.1E-07
Bornholm	22-04-2010	1.1E-11	9.5E-05	1.2E-07

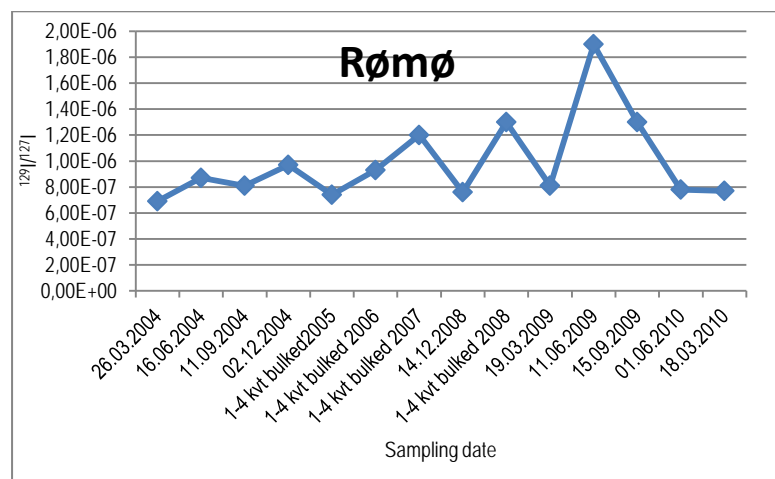


Fig. 2 Temporal variations of $^{129}\text{I}/^{127}\text{I}$ in *Fucus Vesiculosus* collected from Rømø.

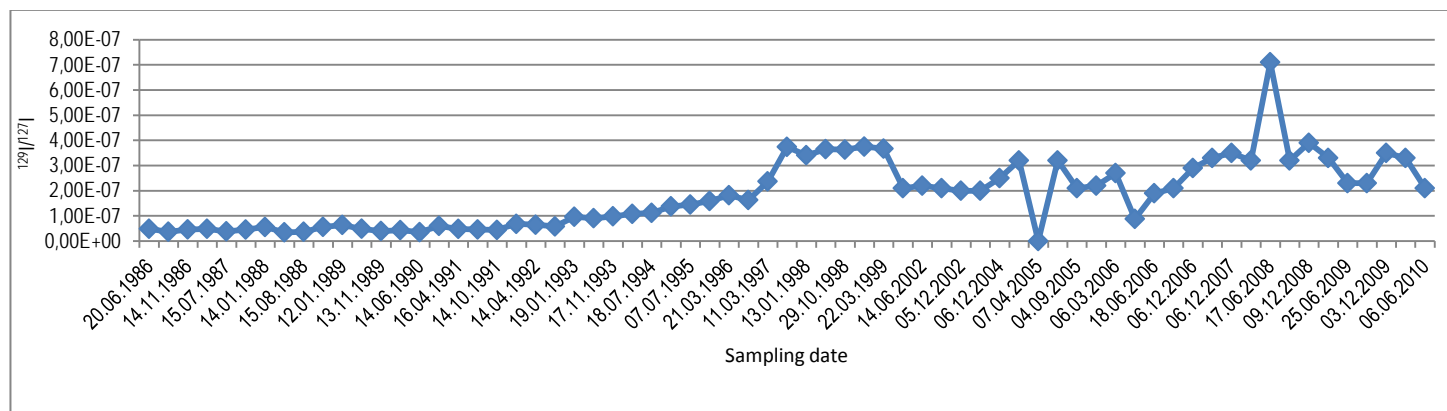


Fig. 3 Temporal variations of $^{129}\text{I}/^{127}\text{I}$ in *Fucus Vesiculosus* collected from Klint. The ratios of $^{129}\text{I}/^{127}\text{I}$ in *Fucus* collected from 1986 to 1999 are reproduced from Hou et al., 2000. The ratios of $^{129}\text{I}/^{127}\text{I}$ in *Fucus* collected from 2002 to 2010 are from present study.

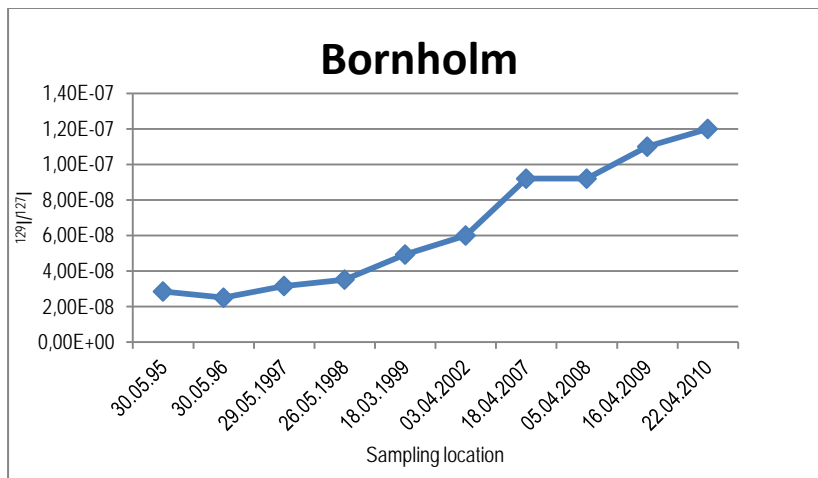


Fig. 4 Temporal variations of $^{129}\text{I}/^{127}\text{I}$ in *Fucus Vesiculosus* collected from Bornholm. The ratios of $^{129}\text{I}/^{127}\text{I}$ in *Fucus* collected from 1995 to 1999 are reproduced from Hou et al., 2000. The ratios of $^{129}\text{I}/^{127}\text{I}$ in *Fucus* collected from 2002 to 2010 are from present study.

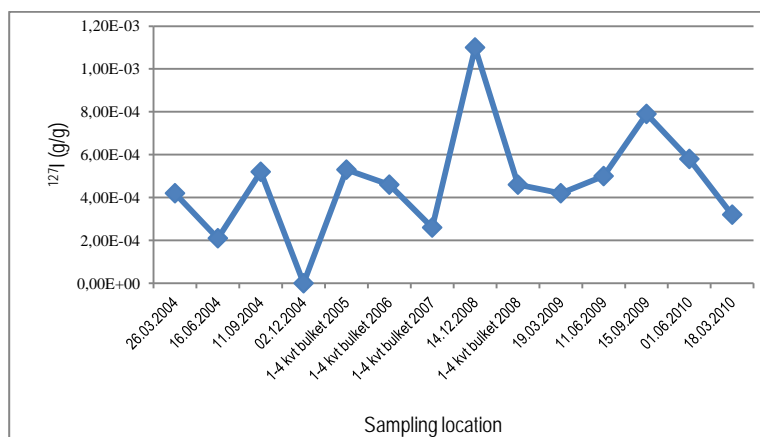


Fig. 5 Temporal and sesonal variations of ^{127}I in Fucus Vesiculosus collected from Rømø.

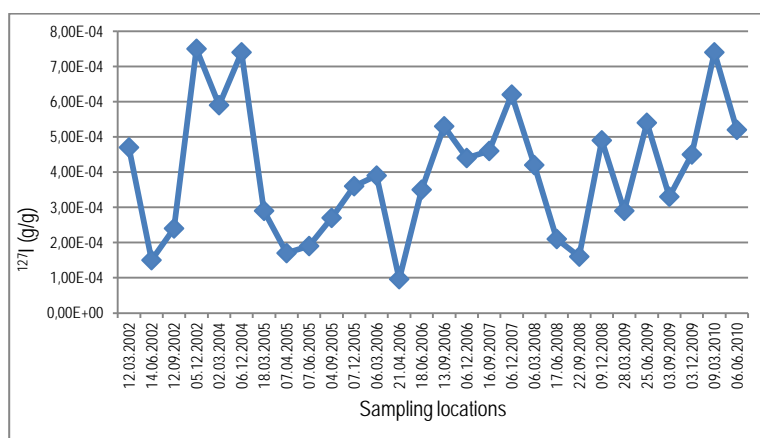


Fig. 6 Temporal and seasonal variations of ^{127}I in Fucus Vesiculosus collected from Klint.

Acknowledgements

The authors would like to thank Svend Olsen and Claus Bang for collecting the studied samples. VH is grateful to the Radioecology and Tracers Programme (headed by Sven P. Nielsen) at the Radiation Research Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, for supporting her Ph.D. project.

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Paper VI

Hansen Violeta. 2011. Iodine (^{129}I and ^{127}I) speciation in freshwater samples from Denmark and Sweden, Manuscript

Iodine (^{129}I and ^{127}I) speciation in lakes from Denmark and Sweden

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Abstract

We here present the first data on the abundance of the iodide and iodate and organic iodine species of the ^{129}I and ^{127}I isotopes in lakes located in south Jutland (Denmark) and southeast Sweden. Excepting the Skærsø Lake, where the organic iodine – ^{127}I accounts for 50% of the total iodine, the iodide (both ^{129}I and ^{127}I) is the predominant species form in surface water of the studied lakes. Iodine-129 concentrations in the lakes ranged from $1.3 - 12.8 \times 10^9$ at/L and show elevated concentrations in lakes located in southwest Jutland (Denmark), near the North Sea. Further the ^{129}I concentration in the studied lakes may be dominated by the continuous supply to the marine environment from the nuclear fuel reprocessing plants (La Hague (France) and Sellafield (U.K.)) and subsequent redistribution through precipitation and to a lesser extent to atmospheric releases from reprocessing plants, volatilization from soils and plants and release for lakes sediments.

Key words: ^{129}I , ^{127}I , chemical speciation, lake, AMS, ICP-MS

1. Introduction

In nature iodine – 129 occurs naturally, but mainly originates from anthropogenic nuclear activities such as nuclear reprocessing facilities, nuclear weapons testing and accidents associated with nuclear power plants. Its concentration has been and is still increasing in the environment since the beginning

of the atomic era in the late nineteen forties (Englund et al., 2010; Aldahan et al., 2007). Iodine is an element with multiple oxidation states -1,0,+1,+3, +5 and +7, forming a wide variety of chemical compounds in natural environmental Eh-pH conditions (Hou et al., 2009; Liu and Gunten, 1988). In aqueous systems iodine occur as ioide (-1) and iodate (+5) with a minor amount of organic iodine in seawater but considerable amounts in freshwater systems (Wong, 1991; Wong and Zhang, 2003). Attempts to explain the reduction of iodate to iodide in seawater have demonstrated (Tsunogai and Sase, 1969) that certain organisms enzymatically (nitrate-reductase) are able to reduce iodate to iodide while another study (Waite and Truesdale, 2003) has not found the same results. Campos et al., (1999) indicated that there might be a linkage between the iodide production and nitrate concentration, showing that the iodide levels were increased as nitrate concentrations decreased. Through observations of the iodate-iodide redox behavior in North Sea surface water samples, Spokes and Liss (1996) showed that iodide is photochemically produced by iodate reduction and that organic matter plays an important role in the process.

The oceans and seas are considered the main reservoirs of iodine in the Earth's surface (Fuge & Johnson, 1986) and the sources of iodine in the terrestrial environment such as soils and lakes originate mainly from the seas and oceans through transport of atmospheric iodine species and subsequent redistribution onto the earth's surface environment by precipitation. Whereas 92% of ^{129}I occur as iodide, iodate-127 accounts for 43 – 93% of total iodine in archived precipitation samples collected during 2001-2006 in Roskilde, Denmark (Hou et al., 2009b). Iodine speciation analysis in lakes samples has not been so numerous. Jones et al., (1984) detected both, iodide-127 and iodate-127 in some British lakes and reported a reduction of iodate during spring and summer and oxidation of iodide during autumn and winter. The authors suggested that the algae with active nitrate reductase are responsible for iodate reduction during the spring and summer while iodide is oxidized in the surface

water in winter by molecular oxygen. Investigating the speciation of inorganic iodine in a water column of Rogoznica Lake, Zic & Branica (2006), showed that iodate concentration fall in the summer while an opposite behavior were occurred for iodide. The enrichment of iodide in this lake was explained as a result of bacterial and chemical processes as well as releases from sediments.

The chemical behavior of iodine and the extent with which it is able to be trapped by soils and sediments or released into the atmosphere from lakes are mainly determined by its physico-chemical forms, i.e. speciation, and lesser extent by their gross concentrations.

Despite the common incorporation of iodine in many biogeochemical cycles and the occurrence of high levels of anthropogenic iodine-129 in the studied area there are no data on the chemical speciation of ^{129}I in these lakes waters and so far there are relatively few data on the chemical speciation of ^{127}I in lakes. Therefore, addition of lake water data sets will certainly expand our understanding of the iodine cycle in general and the radioactive isotope in particular. This study aims to investigate: (1) the concentration and chemical speciation of iodine (both isotopes) in surface lake water and (2) the possible sources of anthropogenic iodine in studied regions.

2. Samples and analytical methods

Samples and Reagents. Surface lake water (1L) were collected from 9 sampling sites in Denmark and 5 sampling sites in Sweden in 2007 (Figure 1). The sampling locations of the investigated samples are presented in Tables 1-2. The samples were filtered through a $0.45\ \mu\text{m}$ membrane (Sartorius AG, Gottingen, Germany), tightened and stored in clean polyethylene containers in dark conditions until analysis. All chemical reagents used were of analytical grade, and all solutions were prepared using deionized water ($>18.2\Omega$). A diluted ^{129}I standard (prepared from NISTSRM 4949C) with a $^{129}\text{I}/^{127}\text{I}$

ratio of 1.1×10^{-11} , ^{125}I tracer (Amersham Pharmacia Biotech, Little Chalfont, Buckinghamshire, UK), ^{127}I carrier (Woodward iodine, MICAL Specialty Chemicals, New Jersey) and Bio-Rad AG1- \times 4 anion exchange resin (Bio-Rad laboratories, Richmond, CA) were used.



Fig. 1 Sampling locations for Lakes collected from Denmark and Sweden

Separation of iodine species as iodide and iodate. A modified version of the analytical method of Hou et al. (2007) was used for the separation of different species of iodine. Bio-Rad AG1- \times 4 strongly basic anion exchange resin, 50–100 mesh, converted to NO_3^- form was packed in a column of $\phi 1.0 \times 20$ cm. 100-300 mL of lake water spiked with about 50 Bq of ^{125}I tracer was loaded onto the column at a flow rate of 1 ml min^{-1} , and the column was washed with 30 mL of distilled water and then 50 mL of

0.2 M KNO_3 . The effluent and the washes were combined for the determination of iodate. Iodide on the column was eluted using 40 mL of 10% NaClO .

Total iodine including organic and inorganic species determination. To a certain volume of fresh water sample (100 mL) spiked with about 50 Bq of $^{125}\text{I}^-$ tracer, 5mL of 15% NaClO and 5mL of 3M NaOH was added. This mixture was heat at $150\text{ }^{\circ}\text{C}$ for 3h.

Extraction of iodine from all separated fractions. About 50 Bq of a $^{125}\text{I}^-$ solution was added to effluent plus wash from the anion exchange chromatographic separation procedure above (iodate fraction) as chemical yield tracer. About 2.0 mg of stable iodine (prepared from Woodward iodine) was added to all separated fractions as a carrier. To convert all iodine to iodide, 0.2 mL of 2.0 M NaHSO_3 was added and pH was adjusted to 2 using 3.0 M HNO_3 . Iodine was first extracted with CCl_4 after oxidation of iodide to molecular iodine using NaNO_2 , and then back-extracted with NaHSO_3 solution. The extraction and back-extraction was repeated to purify the iodine solution. The chemical yields of iodide and iodate were measured by counting ^{125}I in the separated solution using a $\text{NaI } \gamma$ -detector, and were found to be 50-70% and 72-98% respectively. The chemical yields of total iodine were found to be 44-92%.

^{127}I and ^{129}I preparation for ICP – MS and AMS measurement. One milliliter of iodide fraction was taken and diluted to 20 mL with 0.1 M NH_4OH . About 10 mL of original lake water and 10 ml from iodate fraction was taken and NH_4OH solution was added to a NH_4OH concentration of 0.1 M. Cs^+ as (CsCl) was added as an internal standard to a concentration of 2.0 ng/mL. The concentration of ^{127}I was determined using an X-SeriesII ICP-MS (Thermo Electron Corporation). The detection limit, calculated as 3SD of blanks, was 0.23 nM.

Iodine as iodide in the final back extracted solution was transferred to a centrifuge tube, and 1.5mL of 3M HNO₃ was added. To the solution 1mL of 1M AgNO₃ was added and mixed. The AgI precipitate was finally dried at 60-70 °C, and then ground to powder. The silver iodide was mixed with niobium powder and pressed into a copper holder for measurements of ¹²⁹I by accelerator mass spectrometry (AMS) at the Tandem Laboratory, Uppsala University using a terminal voltage of 3.5MV. The statistical error of the analysis including mainly measurement errors at 1 standard deviation was <10%, as blank correction was negligible.

Results

The concentrations of ¹²⁹I and ¹²⁷I (as iodide, iodate and total iodine) and their ratios are listed in Tables 1-2. The concentration of stable iodine varies from 2.6 to 35.6 µg L⁻¹ in Danish lakes and 4.8 to 7.6 µg L⁻¹ in Swedish lakes. The ¹²⁷I-iodide show some spatial difference with a maximum about 35.5 µg L⁻¹ in the Dybesø Lake located near south Kattegat and the minimum of 2.6 µg L⁻¹ in the Karlsgårdesø Lake near North Sea (Table 1 and Figure 1). The ¹²⁷I-iodide is the dominant iodine speciation in samples measured here. Unlike ¹²⁷I-iodide the distribution of ¹²⁷I-iodate seems rather homogenous in the surface water of the studied area. On an average there is less iodate in lakes collected from Denmark when comparing with the lakes located in southern Sweden (Table 2 and Figure 1). The situation for the distribution of ¹²⁹I speciation seems homogenous for ¹²⁹I-iodide where a decrease in concentrations follows the distance from the North Sea. Similar to the behavior of ¹²⁷I, the ¹²⁹I-iodide is the dominant speciation compared to iodate. Maximum value of ¹²⁹I-iodide 15.1 ×10⁹ at/L in Fåresø Lake collected near North Sea, whereas the minimum value is around 1.8 ×10⁹ at/L and occurs in the Dybesø Lake located near south Kattegat. For the ¹²⁹I-iodate the range for minimum and

maximum values is at $0.03\text{-}0.06 \times 10^9$ atoms/L and $0.5\text{-}0.7 \times 10^9$ atoms/L in the studied lakes (Tables 1 and 2).

Discussion

Because of the low concentration of organic iodine encountered in seawater, recently works on speciation analysis in seawater are focused on iodide and iodate while organic iodine being calculated as difference between the total inorganic iodine and total iodine. Although high concentrations of organic iodine have been reported in fresh water compared to seawater (Reifenhäuser and Heumann, 1990), studies concerning quantification of aquatic organic iodine are still very limited. Photochemical decomposition (H_2O_2)/UV or dehydrohalogenation (NaOH/ ethanol) of aquatic organic iodine has been previously employed (Wong & Cheng, 2001; Schwehr, 2003) and the results show a discrepancy of up to 40% or higher, depending on methods. Photochemical decomposition (H_2O_2)/UV of dissolved organic iodine in seawater have shown to produce iodide (Wong & Cheng, 2001). A question of whether photochemical destruction of organic matter occurs in the same time with formation in small proportion of iodine organic matter remains uncertain (Wong & Cheng, 2001; Moore & Zafiriou, 1994).

Conventional, organic matter destruction can be performed by hydrolysis, reductions, thermal and wet oxidation and thermal methods (Stevenson, 1994). Oxidation methods include oxidizing agents, such as potassium permanganate (KMnO_4), disodium peroxodisulphate ($\text{Na}_2\text{S}_2\text{O}_8$), or sodium hypochlorite (NaOCl). In this study the iodine organic matter was destroyed by using NaClO in alkaline medium at 150°C for 3h. Excepting few locations in Denmark were organic iodine-127 accounts for 50% of the total iodine-127 and the precipitation sample collected from Rasback, Sweden the iodine (both isotopes) associated organic matter calculated by subtracting inorganic iodine (iodide + iodate) from

total iodine (Tables 1-2) were not detected. Those results may be partly attributed to decomposition of NaClO occurred while increasing the temperature (in this study 150⁰C for 3h). Due to this a part of iodine organic matter in those samples may not destroyed. The results further indicate iodide (both isotopes) as a predominate speciation form in surface water of the studied lakes with a low amount of organic iodine.

A similar speciation pattern of stable and anthropogenic iodine as reported in this study were occur along the surface water of the Baltic Sea (Hansen et al., 2011), iodide being the dominant specie of iodine. By contrast in southwest North Sea, the $^{129}\text{I}/^{129}\text{IO}_3^-$ values ratios varies from 0.9 to 1.6 (Hou et al., 2007). Furthermore speciation analysis of iodine (both isotopes) in archived precipitation samples collected from Roskilde, Denmark indicated iodide – 129 and iodate – 127 as dominant forms with lower (19% of the total iodine) amount of organic iodine (Hou et al., 2009b).

The results of this study are noteworthy and reflect that the general trend in speciation of the two iodine isotopes is, to a large extent, linked to environmental conditions of fresh water such as flushing time, pH, Eh, content and quality of organic matter, microbial activity as well as differences in contaminant origin and chemical speciation of both isotopes deposited on the terrestrial environment.

In the studied area the ^{129}I sources in lake waters include, apart from natural occurrence, fallout from atmospheric nuclear weapon tests, the Chernobyl accident, releases from nuclear power plants and discharges from nuclear fuel reprocessing plants. Contributions of ^{129}I from nuclear weapon tests, Chernobyl accident and nuclear power stations to the investigated area are comparatively insignificant (Hou et al., 2007; Aldahan et al., 2006). Nowadays, the nuclear reprocessing facilities La Hague (France) and Sellafield (U.K.) are the main contributors to the European ^{129}I release. By 2007, atmospheric releases from these plants have been 75 and 180 kg, respectively (Hou et al., 2009). During this time period, respectively 3800 and 1400 kg of ^{129}I (Hou et al., 2009) have been discharged

into the English Channel from the La Hague reprocessing plant and to the Irish Sea from the Sellafield reprocessing plant. Hou et al., (2009b) have shown that the contribution of iodine – 129 originating from atmospheric release from those reprocessing facilities might be less important to the iodine – 129 in archived precipitation samples collected from Roskilde, Denmark, leaving mainly the reemission of ^{129}I from the North Sea as the significant source in European precipitations. Furthermore our data show an enrichment in ^{129}I in lakes collected from Engso, Faerso and Skærso, located near North Sea, southwest Jutland, when comparing with those collected from southern Baltic Sea and Sweden (Tables 1 and 2). Comparatively with our results, the values of ^{129}I concentrations were one order of magnitude lower (Reithmeier et al., 2007) in various lakes located in Europe and Russia, far away from reprocessing facilities La Hague (France) and Sellafield (U.K.).

In the present study the ^{129}I concentration in the studied lakes may be dominated by the continuous supply to the marine environment from the nuclear fuel reprocessing plants and subsequent redistribution through precipitation and to a lesser extent to atmospheric releases from reprocessing plants, volatilization from soils and plants and release for lakes sediments.

Table 1 Analytical results of ^{129}I and ^{127}I as iodide and iodate and total iodine in fresh water samples collected from Denmark

Sampling date	Sampling locations	Coordinates	^{127}I $\mu\text{g iodine L}^{-1}$			^{129}I conc., 10^9 at/L			$^{129}\text{I}/^{127}\text{I}$, 10^{-7} at/at		
			Total iodine	Iodide	Iodate	Total iodine	Iodide	Iodate	$^{129}\text{I}/^{127}\text{I}$	$^{129}\text{I}/^{127}\text{I}$	$^{129}\text{IO}_3^- / ^{127}\text{IO}_3^-$
29/09/07	Engsø	55°37'966"N 08°08'172"E	4.8	4.5	0.03	5.9	7.0	0.06	26.5	33.6	43.2
29/09/07	Grovsø	55°37'775"N 08°11'967"E	2.9	2.3	0.3	6.6	6.7	0.7	49.1	62.9	50.3
29/09/07	Fåresø	55°37'383"N 08°14'335"E	7.6	7.7	0.03	12.8	15.1	0.1	36.3	42.3	71.9
27/09/07	Karlsgårdesø	55°38'708"N 08°34'987"E	2.6	2.8	0.04	1.7	2.3	0.06	14.1	17.7	32.4
26/09/07	Glejbjerg	55°32'749"N 08°50'587"E	5.9	4.6	ND	5.8	6.0	0.06	21.2	28.1	-
26/09/07	Skærsø	55°35'107"N 09°16'643"E	6.1	3.1	0.2	10	10.5	0.4	35.4	73.1	43.2
25/09/07	Rands	55°37'262"N 09°44'375"E	4.9	4.0	0.2	3.4	3.5	0.2	15.0	18.9	21.6
31/10/07	Ulvshale	55°02'933"N 12°14'874"E	5.5	9.8	0.4	5.1	5.1	0.03	20.0	11.2	1.6
31/10/07	Dybesø	55°57'665"N 11°44'674"E	35.6	35.5	0.2	1.7	1.8	0.1	1.0	1.1	10.8

ND: not detected; the iodide and iodate were separated by using Bio - Rad AG1 - \times 4 anion exchange resin while the total iodine-129 and 127 as organic and inorganic iodine were obtained by oxidation of organic matter using NaClO in alkaline medium at 150°C for 3h.

Table 2 Analytical results of ^{129}I and ^{127}I as iodide and iodate and total iodine in fresh water samples collected from Sweden

Sampling date	Sampling location	Coordinates	Sample type	^{127}I $\mu\text{g iodine L}^{-1}$			^{129}I conc., 10^9 at/L			$^{129}\text{I}/^{127}\text{I}$, 10^{-7} at/at		
				Total iodine	Iodide	Iodate	Total iodine	Iodide	Iodate	$^{129}\text{I}/^{127}\text{I}$	$^{129}\text{I}/^{127}\text{I}$	$^{129}\text{IO}_3^- / ^{127}\text{IO}_3^-$
12/09/07	Ringsjön	55° 52' 17.69'' N 13° 30' 34.24'' E	Lake	7.6	7.6	0.3	1.9	1.9	0.02	5.4	5.4	1.4
12/09/07	Ivösjön	56° 09' 22.99'' N 14° 23' 03.97'' E	Lake	6.2	8.2	0.2	1.8	2.4	0.03	6.3	6.3	3.2
03/09/07	Hagbyån	56° 38' 59.83'' N 15° 52' 10.46'' E	River	6.4	8.5	0.2	1.3	1.3	0.04	4.4	3.3	4.3
04/09/07	Saleboda	56° 28' 32.11'' N 15° 34' 40.61'' E	Lake	6.5	6.4	0.3	1.9	2.3	0.05	6.3	7.8	3.6
04/09/07	Råsbäck	56° 38' 15'' N 16° 2' 16'' E	Rain	4.8	3.5	0.3	3	4	0.2	13.5	24.7	14.4

The iodide and iodate were separated by using Bio-Rad AG1- \times 4 anion exchange resin while the total iodine-129 and 127 as organic and inorganic iodine were obtained by oxidation of organic matter using NaClO in alkaline medium at 150°C for 3h.

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